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The Preparation, Characterization, and Condensation Reactions of Polymer-Supported Lignin Models

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THE PREPARATION, CHARACTERIZATION, AND CONDENSATION REACTIONS OF POLYMER-SUPPORTED LIGNIN MODELS

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SUMMARY

Lignin condensation and fragmentation reactions compete during the alkaline pulping of wood. Condensation is a counterproductive reaction in which new lignin-lignin bonds are formed; the ensuing interunit linkages are stable under high temperature alkaline conditions. The condensed material is thought to contribute to the final structure of residual lignin — a lignin that cannot be removed during pulping without extensive pulp yield and quality losses.

Soluble model compounds have frequently been adopted to examine the mechanisms of condensation. Model compounds are well suited for such work since they provide a well defined reaction system. Soluble systems do not, however, model any of the polymeric properties of lignin, nor do they provide the heterogeneous reaction environment typical of most pulping sequences. Reactions involving an isolated lignin or wood, although realistic, often lead to products that are difficult to characterize.

Polymer-supported lignin models overcome these problems. The insoluble models, in which simple lignin structures are attached to macroreticular polystyrene resins, simulate the heterogeneous pulping environment of lignin while retaining the defined structure of their soluble counterparts.

It was the objective of this thesis to use supported lignin models to evaluate condensation reactions that are believed to play a key role in generating residual

lignin during alkaline pulping. The degree to which the supported lignin moieties undergo condensation with soluble reactants was examined relative to that of analogous, but completely soluble, systems. The reactions of a phenol derived carbanion with a quinone methide (QM) were selected as representative of condensation ongoing during alkaline pulping; two heterogeneous systems were studied in which either the carbanion or the QM was immobilized on the resin support.

For the first heterogeneous model, the ligninlike monomer guaiacylpropanol, 3-(3'-methoxy-4'-hydroxyphenyl)propan-1-ol, was attached at the gamma carbon through a benzyl ether linkage to a modified Amberlite XE-305 resin. The phenolic site of guaiacylpropanol was protected as an allyl ether when coupled to the resin. The model loading was determined by cleaving the benzyl ether linkage with iodotrimethylsilane and measuring the amount of released guaiacylpropanol. Spectral characterization of the resin intermediates and product by FTIR and high resolution ^{13}C-NMR confirmed the chemical analyses of the heterogeneous model. An x-ray analysis showed that the distribution of model throughout the resin was homogeneous.

Reactions of the supported guaiacylpropanol with the soluble QM of syringyl alcohol were studied. For comparative purposes, reactions of the QM with guaiacylpropane, the soluble analog of the bound guaiacylpropanol, were also evaluated. Guaiacylpropane readily coupled to the QM of syringyl alcohol in sodium hydroxide at 170 °C to give a C5-Cα dimer. The yield of insoluble condensation product was

28% of the level of soluble C5-Cα dimer. The quantity of C5-Cα dimer formed in the two-phase system exceeded expectations since the soluble co-dimerization species, syringyl alcohol, had several alternative "soluble" pathways for consumption. The data suggest that soluble lignin units are capable of condensing onto the insoluble lignin gel during the course of an alkali cook.

A second heterogeneous model, which contained a simple guaiacyl-type appendage capable of forming a QM in alkali, was joined to the resin through a benzyl ether linkage. The synthetic procedure required nine steps and involved several protecting group methodologies. Model loading determinations and spectral characterization of the insoluble model were conducted as described above.

The analogous soluble QM, when reacted under soda pulping conditions, rapidly underwent condensation with a ligninlike nucleophile (2,6-dimethoxyphenol), yielding a C1-Cα dimer. No dimer was observed in the heterogeneous QM system, which suggests that steric constraints imposed by the resin may be prohibiting reaction. Reactions of the supported models were shown not to be mass transfer limited. These results imply that condensation of dissolved lignin moieties onto the lignin gel may not occur until later in the cook when a higher degree of accessibility has been attained.

Overall, the condensation results of both polymer-supported models confirm a lower degree of reactivity in heterogeneous systems and indicate that reactions of soluble models may be poor predictors of many pulping reaction rates.

INTRODUCTION

PERSPECTIVE

Pulping processes are ideally designed to selectively remove the cellulosic fibers from the wood matrix. The fibrous mass then serves as the primary constituent in the production of paper and other carbohydrate-based materials. Alkaline pulping processes, in particular the kraft process, have been the predominant means by which wood fibers are isolated. The general premise of the alkaline system is the relatively selective fragmentation of the lignin component of the wood by pulping chemicals. Once the lignin macromolecule has been degraded to a point where it goes into solution, fiber isolation becomes a simple matter of washing away the low molecular weight lignin particles. However, the lignin fragmentation reactions show a degree of reversibility. That is, the fragmented lignin units can couple to each other (condense), resulting in a lignin structure which may be resistant to further pulping.

This investigation has been directed at studying lignin condensation reactions using insoluble polymer-supported lignin model compounds. An enhanced understanding of lignin condensation may eventually lead to a more effective means of prohibiting or minimizing this deleterious reaction thereby improving pulp quality and yields while decreasing costs.

GENERAL OVERVIEW OF ALKALINE PULPING REACTIONS

The constituency of wood, as described by Fengel and Wegener,[1] can be divided into two primary categories, low molecular weight and macromolecular substances. For temperate zone species, the low molecular weight material, which is comprised of extractives and some inorganic matter, accounts for only 1-3% of the total wood material. The macromolecular components, by difference, make up the remaining 97-99% of the wood substrate. The macromolecular entities of wood can be further subdivided into three categories: cellulose, hemicellulose, and lignin.

Cellulose accounts for nearly half of the wood matter and currently serves as the primary source of fiber in the paper industry. Cellulose consists of ordered linear chains of β-D-glucose; the length of these chains in the native state is estimated to be greater that 10,000 units. Hemicellulose, unlike cellulose, contains no regions of crystallinity. Hemicelluloses are comprised of a variety of neutral sugars, one of which may be glucose, in addition to some uronic acids. Furthermore, hemicellulose chains are much shorter than those of cellulose and are often branched to varying degrees.

Lignin, an amorphous material which is deposited between the cellulosic fibrils during biosynthesis, has a completely different chemical formulation than the carbohydrates. Lignin can be viewed as a semi-ordered three dimensional polymeric system of phenylpropane units (Fig. 1). Lignin, like the hemicelluloses, exhibits some structural differences between softwoods and hardwoods. Softwoods, as

shown in Fig. 1, are composed primarily of guaiacyl or 3-methoxy-4-hydroxy-type aromatic nuclei whereas hardwoods contain a predominance of syringyl or 3,5-dimethoxy-4-hydroxy-type nuclei. Also, softwoods generally contain a higher overall percentage of lignin, roughly 28%, compared to the hardwoods which normally are in the 18-20% range.[2]

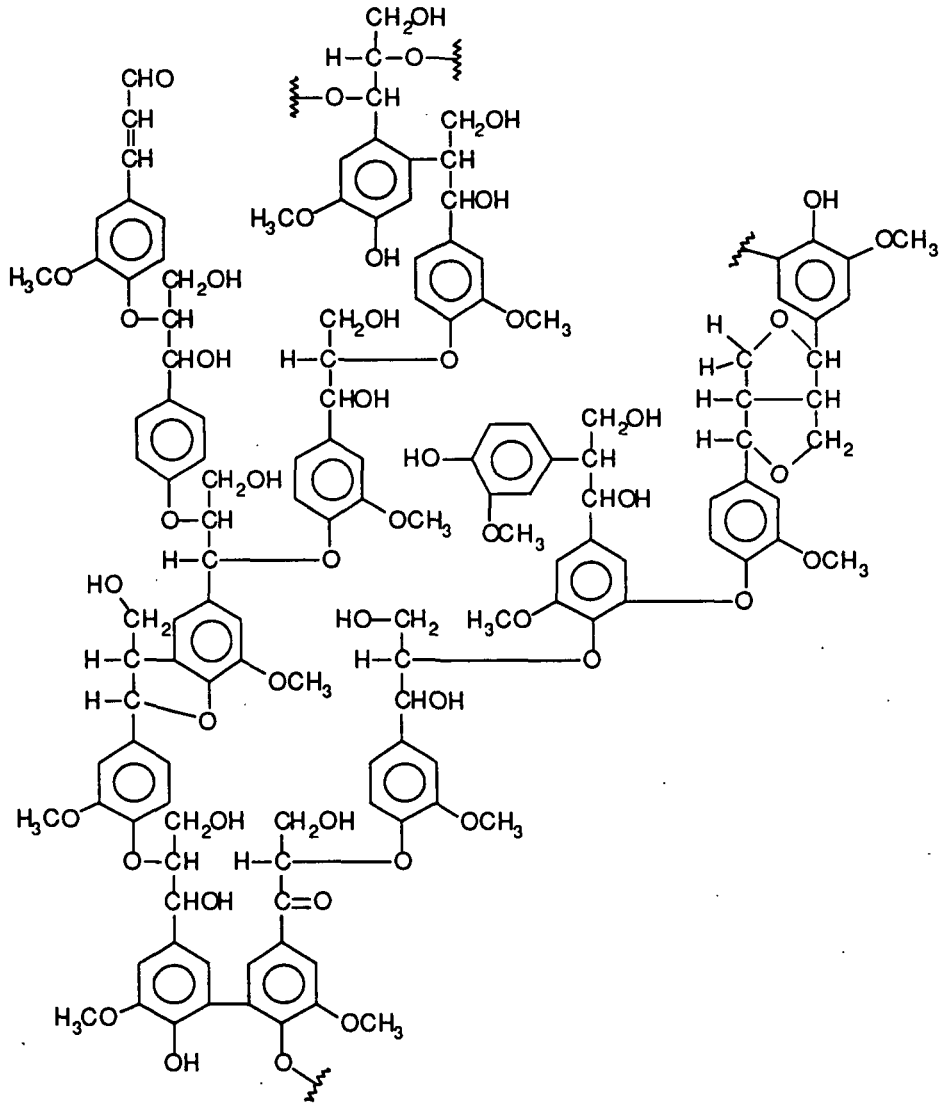


Figure 1. Adler's representation of a softwood lignin.[3] Several other models have been proposed.[4, 5]

Chemical pulping methods are the primary means by which cellulosic fibers are separated from the wood matrix. Alkaline processes, in particular the soda and kraft processes, have been the most prevalent chemical pulping systems employed to date. In both methods the wood is subjected at a high temperature (170 °C) to active pulping reagents, sodium hydroxide (NaOH) or sodium hydroxide/sodium sulfide, respectively. In the ideal chemical pulping operation, the lignin macromolecule would be selectively fragmented and subsequently dissolved in the pulping liquor leaving behind unmodified carbohydrate material. This ideal behavior is approximated by current technology but is certainly not realized to the degree desired.

During the initial phases of pulping, a large proportion of the hemicelluloses, due to their amorphous nature and short, nonlinear structure, are dissolved. Carbohydrate yield losses are due to end-wise peeling reactions in which terminal monomer units are lost.[6] Lignin too can "peel"; this is accomplished by means of the cleavage of labile phenolic α- and β-ether linkages.[7]

During the next phase of pulping, termed the bulk phase, the nonphenolic carbon-oxygen interunit bonds of lignin are severed. This often results in the generation of new phenolic units which further facilitates the breakdown and dissolution of the lignin macromolecule. Cellulose exhibits a similar reaction sequence; glycosidic bond cleavage results in the disruption of the long cellulosic chains hence imparting a reduction in product viscosity.[6]

Pulping is generally not conducted far into its final stage, called the residual phase. The remaining levels of lignin, due to a markedly decreased rate of reaction, cannot be removed without extended carbohydrate yield and viscosity losses.[6-9] The lignin remaining in the pulp after the cook is most often removed in more mild and selective bleaching operations.[10]

Cleavage of interunit lignin-lignin carbon-oxygen bonds is the preferred pulping reaction since it ultimately leads to the breakdown of the wood superstructure thereby freeing the sought after carbohydrate material. Lignin fragmentation reactions are in a sense, reversible. That is, the smaller lignin subunits can couple or condense back together forming higher molecular weight lignin species. Condensation is not, unfortunately, a mere regeneration of the original carbon-oxygen interunit linkages. Instead, the lignin moieties are joined by new carbon-carbon bonds which are more resistant toward the pulping chemicals. The lignin remaining after termination of the cook, referred to as residual lignin, contains a higher percentage of these carbon-carbon bonds than does the original or native lignin. Condensation reactions therefore compete with fragmentation during pulping and appear to contribute, at least in part, to the final composition of the residual lignin.[11-13]

The more relevant aspects of lignin condensation during alkaline pulping will be reviewed in greater detail in the following sections. It should be apparent that future alkaline pulping reagents should inhibit condensation. Minimizing lignin condensation could improve pulp quality and yield. In addition, the

resulting pulp may require a lower degree of bleaching, a factor which could also reduce costs and adverse environmental effects.

LIGNIN CONDENSATION REACTIONS

Model Compound Studies

Model compounds have often been used by researchers to study pulping reactions. Lignin model compounds in particular are typically mono- or dimeric species that represent chosen substructures of the native macromolecule. The precise structure of model compounds makes them ideal for mechanistic studies since specific effects can be readily examined by conventional methods of analysis. Investigations of this sort are difficult with lignin whose exact native structure has not been fully resolved.

The route toward condensation in alkaline pulping systems begins with ionization of the free phenolic sites as demonstrated in Fig. 2 with the ligninlike model vanillyl alcohol. The resulting oxy anions spread their charge through resonance giving rise to several quasi-carbanion forms, which are good nucleophiles. The two most reactive states, the C5 and C1 anions, are depicted along with the initial oxy anion in Fig. 2.[14]

At higher temperatures, reported to be a minimum of 110-120 °C,[15, 16] a quinone methide (QM) can be generated from the C1 anion. In so doing, the oxygen functionality on the α-carbon is lost. The extent of quinone methide formation, at

any given temperature, is related to the nature of the leaving group at the benzylic site. Quinone methides are the primary reactive intermediates in both fragmentation and condensation reactions.[6, 14] In chemically controlled reactions, formation of the QM is the rate limiting step.[17]

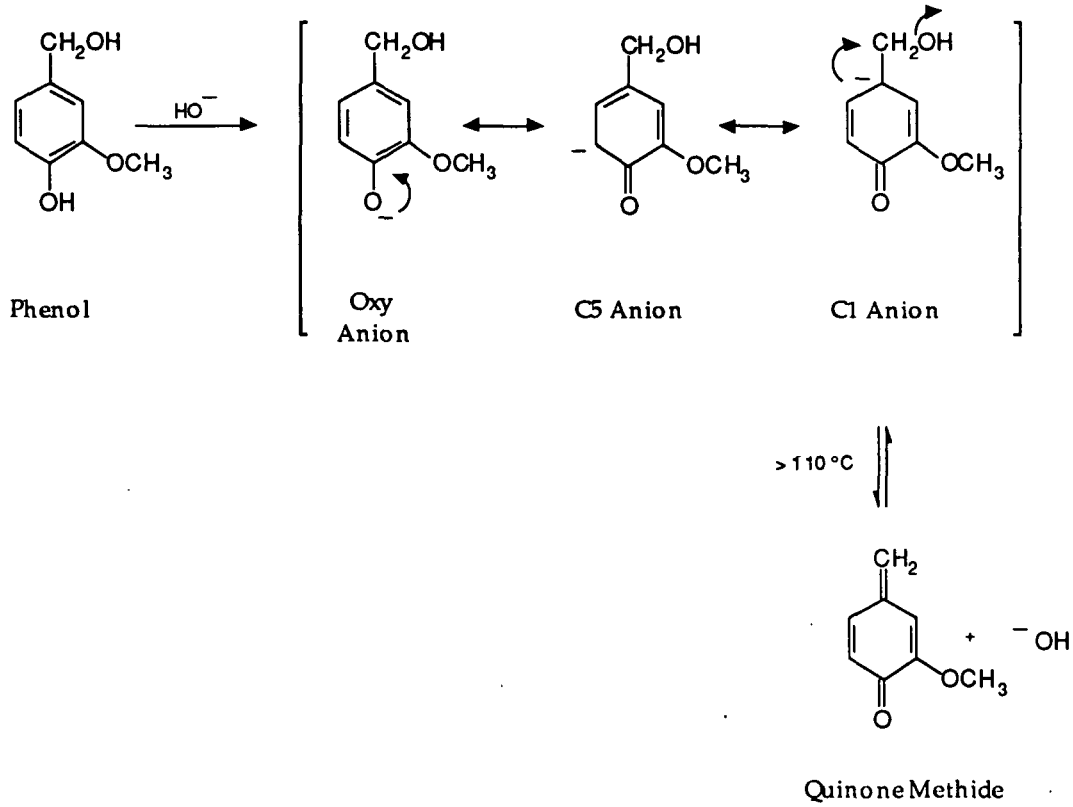
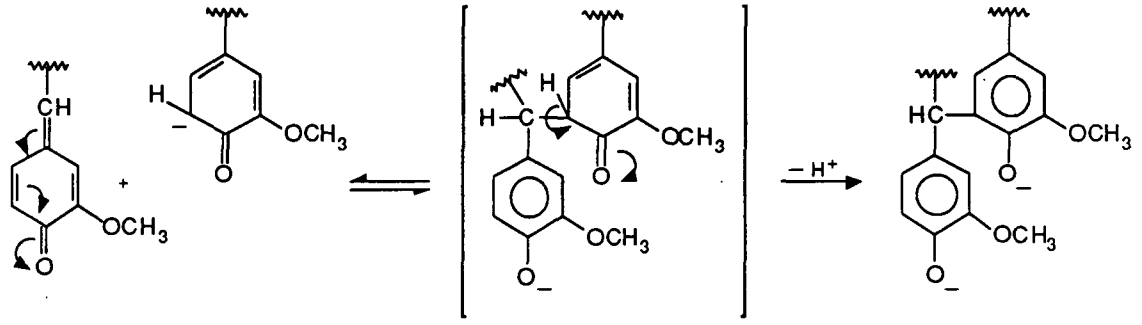


Figure 2. Resonance structures and quinone methide formation in "lignin" under alkaline pulping conditions.[6, 14]

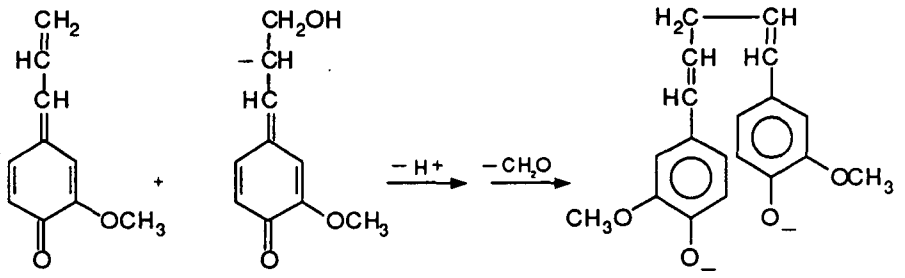
Condensation reactions have traditionally been described in terms of ionic pathways. Certain radical mechanisms may, however, also be operating.[18, 19] Gierer[6, 14] has classified lignin condensation reactions into three (ionic) catagories, primary and secondary condensation, and condensation with formaldehyde (Fig. 3).

The scope of this thesis was limited to the study of primary condensation reaction systems.

(A) Primary condensation



(B) Secondary condensation



(C) Condensation with formaldehyde

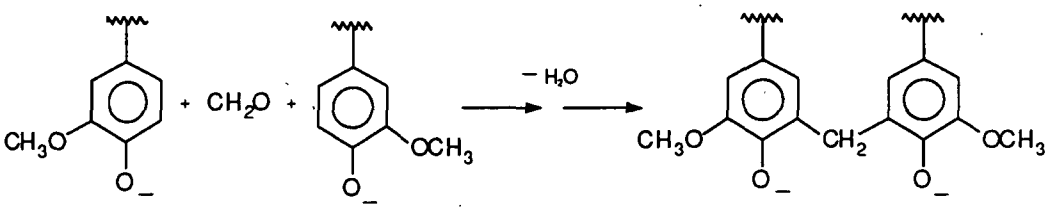


Figure 3. The three major classifications of lignin condensation reactions in alkali: (A) primary, (B) secondary, and (C) condensation with formaldehyde.[6, 14]

As illustrated in Fig. 3, primary condensation involves the reversible addition of a C5 nucleophile to the α-carbon of a QM. The initial coupling step is

followed by an irreversible loss of the C5 proton which allows the attacking nuclei to regain stability through rearomatization of the phenyl ring. This type of condensation leads to the formation of a new C5-Cα carbon-carbon bond. Primary condensation also encompasses the formation of C1-Cα carbon-carbon bonds. The formation of this bond type resembles that of the C5-Cα except that a C1 nucleophile adds onto the QM as depicted in Fig. 4. Deprotonation of the hydroxyl group adjacent to C1 allows for elimination of the side chain as an aldehyde with concomitant rearomatization of the attacking substrate. The diphenylmethane units resulting from primary condensation reactions are relatively stable to further high temperature alkaline pulping transformations.[20]

Model compounds have also been utilized to examine how pulping additives, such as the hydrosulfide ion in the kraft process or anthrahydroquinone (AHQ), promote fragmentation and restrict the extent of condensation.[14, 18] Both reagents couple faster to QMs than do internal lignin carbanions.[17, 21] Occupation of the QM by the additive temporarily prohibits condensation by blocking the approach of a lignin nucleophile. A permanent restraint of condensation occurs if the α-carbon is chemically modified by the pulping additives such that a QM can no longer be generated.[18, 22] The exact nature of how AHQ alters the lignin structure in this regard has not been clearly discerned. Likewise, data comparing the effectiveness of the hydrosulfide anion and AHQ at inhibiting condensation is limited, since most investigations have been concerned with their ability to promote fragmentation reactions.

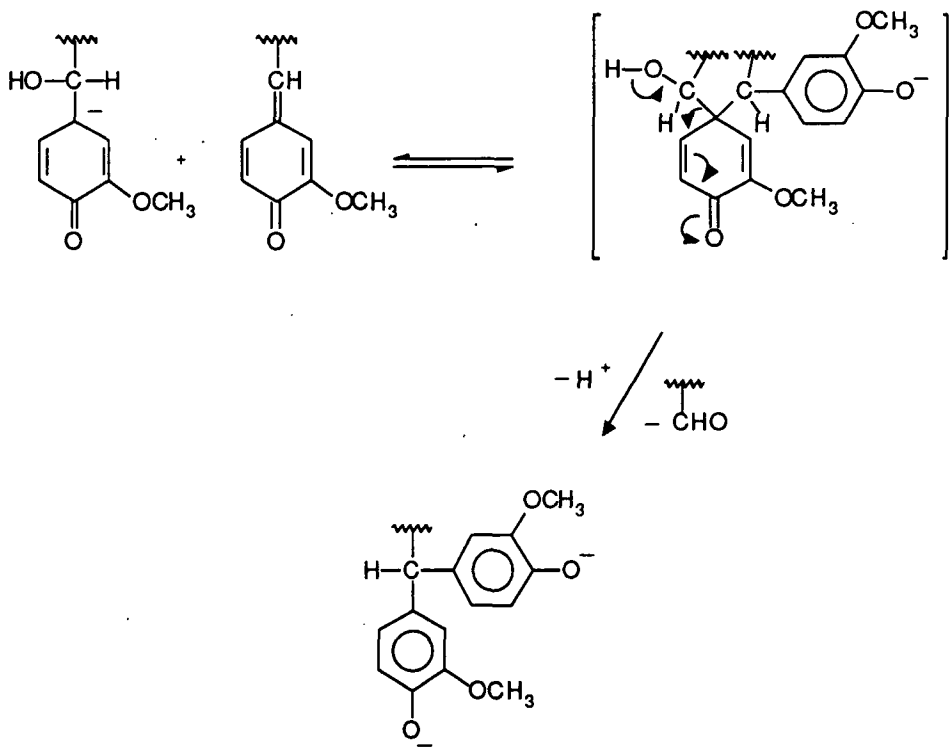


Figure 4. Primary condensation mechanism illustrating the formation of a C1-Cα interunit linkage.[6, 14]

Several other model studies, in addition to those cited above, have been conducted in which the competing fragmentation reactions have been eliminated or controlled, thus revealing the behavior of condensation systems under varying conditions.[23-29] Many of these studies infer that condensation reactions could contribute to the formation of residual lignin. The model studies are limited, however, by their one-dimensional or homogeneous reaction environment. From results of soluble model compound systems, it is difficult to accurately predict the extent of condensation versus fragmentation during pulping, or the extent to which condensation actually contributes to the final structure of residual lignin.

Isolated and Residual Lignin Studies

The structure and size of lignins isolated from spent liquors, or residual lignins in pulp, have been analyzed in an effort to learn more about lignin in its native state and to correlate the reaction pathways suggested by model compound studies. Some emphasis has also been placed on determining how different process variables, such as the type and load of external pulping additives, affect the overall breakdown of the lignin macromolecule. Evidence of alkaline promoted condensation has been detected in several instances within these investigations. Condensation of lignin during pulping is difficult to establish because (a) lignin has a complex chemical structure, (b) native lignin contains a low percentage of condensed units,[3] (c) the distribution of condensed units deviates within the different morphological regions of the cell wall,[30-32] and (d) products resulting from the more prevalent fragmentation reactions often obscure signs of condensed material.

Obiaga and Wayman uncovered some possible evidence of condensation when they monitored the change in molecular weight (MW) of a spruce milled wood lignin (MWL) under simulated kraft and soda pulping conditions.[33] A portion of their data is presented in Table 1. An obvious factor in the soda cook data is the MW increase after 15-30 min at temperature. This increase was ascribed to condensation. Compared to the kraft cook, the condensed soda lignin degraded at a slower rate throughout the remainder of the trial. Condensation may also occur in the kraft system; however, the gel permeation chromatographic (GPC) technique

employed was not sensitive enough to detect any. Reduced levels of condensation in kraft systems are consistent with model compound studies which have shown that the hydrosulfide ion depresses the propensity for interunit coupling during the cook.[14] The limited quantity of kraft condensation was explained in terms of the sulfide species being better than the hydroxide ions in the soda system at stabilizing lignin radicals which had a high potential to combine and form higher MW species.

Table 1. Number average molecular weight (Mn) data of a spruce milled wood lignin cooked under simulated kraft and soda conditions.[33]

Time (min) at 160 °C	Mn Kraft	Mn Soda
0	10,800	10,800
10	8100	
15		8700
30	6200	9000
60	5200	7200
120	4800	6200

A similar study compared the incurred MW changes upon treatment of a pine MWL in soda and soda-AQ* liquors.[35] The soda system again showed some evidence of condensation. As with the hydrosulfide ion, AHQ accelerated degradation of the lignin macromolecule leaving no clear sign of condensation. Condensation was more apparent when a dioxane lignin was cooked under soda conditions. The addition of AHQ effectively reduced the degree of interunit coupling but did not completely eliminate it.[36]

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* AQ is the abbreviation for anthraquinone. During pulping, the AQ is reduced by wood polysaccharides to anthrahydroquinone (AHQ), the derivative responsible for promoting lignin fragmentation.[34]

Kondo and McCarthy[37] tested the ability of the soda, kraft, and soda-AQ systems to retard condensation by heating (170 °C) a low molecular weight kraft lignin with coniferyl alcohol, a pulping byproduct that rapidly undergoes condensation,[38] and monitoring the changes in the molecular weight distribution of the mixture at selected time periods. Condensation was prevalent up to 30 min at 170 °C in the soda system after which time fragmentation dominated. The kraft system yielded a lower level of high molecular weight material than the soda-AQ system; both were lower than soda alone.

Nuclear magnetic resonance (NMR) spectroscopy has been often used to probe the structures of isolated lignins for clues as to how the lignin macromolecule is degraded during pulping. The results have not always been in complete agreement. Kwoh et al.,[39] who analyzed an isolated kraft lignin by ^{13}C-NMR, detected a signal associated with diphenylmethane (condensed) moieties; whereas other investigations,[40-43] have not observed any concrete evidence of lignin-lignin condensation. A comparison of the ^{1}H- and ^{13}C-NMR spectra of soda and soda-AQ lignins suggested that AHQ limited the degree of coupling at the aromatic C5 position.[44, 45]

Evidence of condensation has been observed in residual lignins as well. The ^{13}C-NMR spectra of a series of residual kraft lignins indicated that the proportion of condensed units increased with time.[46] Nitrobenzene oxidation and phenyl nucleus exchange methods were combined to determine the extent of formation of diphenylmethane structures in the residual lignins of soda and soda-AQ wheat

straws.[47] Anthrahydroquinone suppressed condensation during the earlier stages of the trial but could not sustain its influence; the final levels of diphenylmethane moieties in the two systems were nearly equivalent. Examination of the residual lignin of a Douglas-Fir cooked under kraft conditions showed that 54% of the remaining phenyl nuclei were associated with diphenylmethane structures.[48] The formation of these structures did not begin until the final pulping temperature (170 °C) was reached.

Analyses of isolated and residual lignins suggest that condensation is not as prevalent as the desired fragmentation reactions. Indeed, this must be the case in order to obtain a pulp with a low lignin content. The minority status of condensation does not deter its importance, however, since the major shortcoming of current pulping technology is the inability to remove the final 3-5% of "residual" lignin; lignin-lignin condensation appears to contribute to the residual lignin content.

Lignin-Carbohydrate Condensation

A discussion of lignin condensation would be incomplete without a brief mention of lignin-carbohydrate condensation. The inability to completely remove (through cellulolytic enzyme treatments) all of the polysaccharide material from an isolated kraft residual lignin led to the conclusion that the resistant carbohydrate matter, primarily hemicellulosic in origin, was covalently bound to the lignin.[49] The existence of native lignin-hemicellulose linkages had been previously

proposed.[50-52] This supposition was extended to explain why lignin-free fibers could not be produced through conventional alkaline pulping procedures.[50, 53] Subsequent studies confirmed the existence of alkali stable lignin-hemicellulose and lignin-cellulose bonds in residual kraft lignin.[54, 55]

Kleinert originally proposed that lignin could possibly "graft" onto cellulose during an alkali cook.[56] That carbohydrates could condense onto nonphenolic lignin moieties via oxirane intermediates was later demonstrated,[57] although the extent to which this happens is thought to be minor.[58]

The phenomena of lignin-carbohydrate condensation during pulping has not been thoroughly scrutinized. The overriding factor which has emerged is that lignin-carbohydrate complexes, either native or condensed, appear to be partially responsible for the resistance of residual lignin to extended pulping.

PULPING REACTION SYSTEMS

Traditional Investigations

As described above, simple mono- or dimeric compounds are often used to study lignin pulping reactions. These model compounds, which emphasize certain functional units of the lignin macromolecule, are advantageous because they provide a well defined system that is easy to characterize and quantify. Model compounds also offer, by choice of the starting materials, a method of studying a particular aspect of pulping while minimizing interfering side reactions.

Isolated lignins or wood currently represent the primary alternative substrates for studying pulping reactions. Obviously, both materials offer a more realistic reaction environment when compared to soluble model compound systems. However, the complex nature of lignin or wood often allows for only a general rather than specific interpretation of data.

Polymer-supported Models

The solid-liquid interface encountered in pulping reactions cannot be ignored since a significant portion of these reactions are believed to occur when lignin is in the gel or solid phase.[12, 40] Indeed, reaction rates in a two-phase system may be influenced by several physical factors beyond the inherent energetics of certain bond types.[59, 60] Thus, the overall rate of pulping reactions can be postulated to be a function of transport, diffusion, adsorption, or desorption phenomena in addition to that of chemical reaction.[61]

The influence of lignin accessibility on reaction rates has been demonstrated in both pulping and bleaching experiments. Bleaching tests have shown that lignin in wood meal reacts at a much slower rate than in soluble model systems where the reactions were instantaneous.[62] Similarly, several studies have shown that the pulping rate can be influenced by the thickness of the wood chip; thicker chips limiting the accessibility of interior concentrations of lignin.[63-65]

The polyelectric behavior of lignin may be another factor involved in defining the rate of pulping. For example, when the hydroxyl groups of lignin are deprotonated by alkali they may electrostatically exclude a further influx of negatively charged ions present in the liquor. This ion exclusion or Donnan equilibrium effect would thus retard further degradation of the lignin macromolecule.[66] Likewise, the reactivity of neighboring groups may be influenced by the electronic configuration of a nearby constituent.[67-70] Such behavior has been observed with polymer-bound carboxylic acid groups in which the pKa of remaining protonated moieties increases as the degree of ionization rises.[70]

Still another factor which is known to reduce heterogeneous reaction rates is a loss in entropy upon formation of the insoluble transition state. This effect has been documented in several organic systems in which significant rate decreases have been detected in two-phase relative to single-phase reactions.[71, 72]

Certainly, soluble lignin models cannot provide any information about the physical aspects of pulping. In this regard, Brunow and coworkers[73] developed an insoluble polymer-supported substrate for examining the efficiency of fungal degradation on a heterogeneous lignin model. This somewhat novel approach was invoked by Apfeld[74] and Bovee[75] for studying lignin and carbohydrate pulping reactions, respectively. Supported, woodlike models provide an avenue for bridging the gap between simple soluble model systems and lignin or wood. The heterogeneous models retain the benefits of the soluble systems, namely, definitive

substrate structure and relative ease of product characterization and quantification. The polymer-supported models go one step beyond soluble models in that they implicate some of the physical phenomena encountered during the pulping of wood: solid-liquid interfaces and a porous insoluble polyionic substrate. Insoluble models will not, however, precisely model the heterogeneous lignin environment. For example, the insoluble models may lack the typical glass transition experienced by lignin during pulping.[76] Also, a nonpolar polystryrene backbone[77] surrounds the immobilized lignin model where, in the lignin gel, a more polar environment exists. Many different effects can be brought about by choice of the insoluble support; one must be aware of the system's limitations.

A macroreticular polystyrene resin was employed as the polymeric support in the preparation of previous insoluble woodlike models.[74, 75] Polystyrene, which is commercially available in a wide range of morphologies, is often chosen as a supporting network because the aromatic nuclei are easy to chemically modify while the aliphatic backbone generally is not.[78, 79] Polystyrene resins, which have a high degree of thermal stability (220 °C),[80] are ideal as pseudo lignin matrices since, like lignin, they are crosslinked aliphatic-aromatic polymers. Macroreticular resins in particular consist of agglomerates of microgels as shown in Fig. 5.[80, 81] The macropores, or interstices between the microgels, are accessible to all solvents. Unlike the macropores, the interior regions of the microgel particles are accessible only in the presence of a good swelling agent. It should be noted that solvents which swell the gel matrices to a greater degree afford a higher mobility to the substrates bound to

them.[82] The permanent macroporous network makes the macroreticular resins ideal for wood model supports since the eventual pulping reactions will be occurring in hot alkali, a solvent that should not readily penetrate the microgel environment. Other classifications of polystyrene supports, micro- and macroporous gel-type resins, which are commonly utilized as synthetic reagents, do not provide extensive access to aqueous reagents and are therefore not well suited for pulping applications.

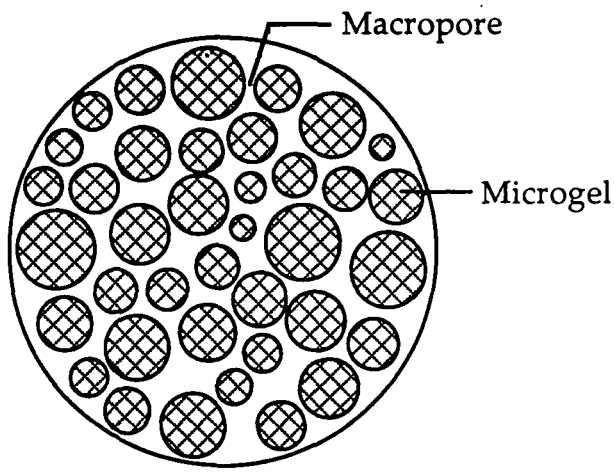


Figure 5. Cross-sectional view of a macroreticular polystyrene resin.[80]

THESIS OBJECTIVES

Lignin condensation during pulping has been an elusive reaction to characterize and quantify owing to the complex nature of wood and interference from competing fragmentation reactions. Polymer-supported lignin models are powerful experimental tools for studying condensation reactions since they exploit the definitive chemical structure of soluble compounds while simulating the physical phenomena encountered during the heterogeneous reactions found in pulping. Insoluble models have not yet been employed in the study of lignin condensation reactions.

The objective of this thesis was to ascertain the relative extent of primary-type condensation, under soda pulping conditions, between analogous hetero- and homogeneous lignin model systems. Inherent in this objective was the preparation of two polymer-supported ligninlike phenols that in alkali would subsequently form a carbanion or a QM which could then react with a soluble QM or nucleophile, respectively. These results should further elucidate the likelihood that lignin condensation reactions contribute to the formation of residual lignin.

RESULTS AND DISCUSSION

EXPERIMENTAL APPROACH

Primary-type lignin-lignin condensation between a phenol derived carbanion and a QM that leads to the formation of alkali stable carbon-carbon bonds could involve the following phases:

soluble phenol + soluble QM ⟶ soluble or insoluble condensed product [1]

insoluble phenol + soluble QM ⟶ insoluble condensed product [2]

soluble phenol + insoluble QM ⟶ insoluble condensed product [3]

insoluble phenol + insoluble QM ⟶ insoluble condensed product [4]

This thesis addresses the likelihood of reactions [2] and [3], in comparison to analogous soluble-soluble interactions. The first reaction, leading primarily to alkali soluble products, has been extensively studied. Reaction-type [4] should have a low probability of occurrence, unless the two gel-phase partners happen to have a close proximity.

Several projects were completed prior to performing the desired condensation reactions:

(a) evaluation of supporting macroreticular polystyrene resins for synthetic and diffusion characteristics,

(b) preparation and characterization of appropriate insoluble lignin models, either as a supported phenol or QM, and

(c) synthesis of the corresponding soluble model counterparts.

The discussion of results will follow this order.

THE HETEROGENEOUS SUPPORT

Evaluation of Supporting Resins

Amberlite XE-305 was employed as a supporting matrix in previous heterogeneous lignin[74] and carbohydrate[75] model syntheses. A large, permanent pore diameter (1400 Å)[83] makes this Amberlite resin an attractive support for working in poor solvent systems such as aqueous alkali. On the other hand, Amberlite XE-305, due to its light crosslinking (3-4%), swells in good organic solvents, a feature which is quite useful in synthesis.[79, 84, 85] Furthermore, the resin has shown only minor signs of deterioration when cooked in 2.5M alkali at 170 °C for five days.[75]

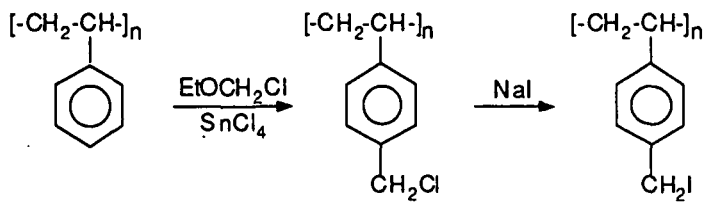
A second macroreticular resin (Biobead SM-16) was also investigated for potential use. Table 2 compares the physical properties of Amberlite XE-305 to those of SM-16. As shown, the SM-16 resin is more highly crosslinked, which imparts limited swelling along with a much smaller pore diameter (144 Å) and larger specific surface area (860 m^2/g).[81, 86, 87] It was envisioned that the SM-16 would provide a more dimensionally stable support that had a large concentration of attached model on the outer edges of the resin thus making them more accessible to alkaline pulping reagents.

Table 2. Physical characteristics of polymeric supports.[83, 88]

	Amberlite XE-305	Biobead SM-16
Cross-link Ratio (%)	3-4	16
Ave. Pore Diam. (Å)	1400	144
Surface Area (m^2/g)	48	860
Swellability	Good	Limited

Highly crosslinked resins are noted for limited degrees of reactivity.[84, 86] Although the SM-16 resin possessed desirable physical properties, it was anticipated that low synthetic yields would be imposed, since resins with higher surface areas are generally less active than resins with large pore diameters.[89] Moderate to low (0.2 - 0.4 mmol/g)* loading yields were reported in previous work[74, 75] with Amberlite XE-305, a resin that typically has potential, being of a lighter crosslinking ratio and thus more accessible phenyl nuclei, for higher synthetic yields. For synthetic evaluation, the two resins were derivatized in a two-step process to benzyl iodides as shown in Scheme 1. Elemental analysis for the halides was used to determine the success of each transition.

Scheme 1



1 2 3

* mmol of model per gram of resin

After being washed to remove surface impurities,[90] the two resins (**1**) were functionalized to benzyl iodides (Scheme 1). The iodides (**3**), which were prepared according to the Finkelstein reaction[91, 92] from the corresponding chlorides (**2**),[93a] were sought to give greater S_N2 reactivity[94a] during subsequent synthetic reactions.

As shown in Scheme 1, para substitution is the dominant position of chloromethylation.[95] Depending on the catalyst and reaction conditions, several side reactions can occur during chloromethylation.[89, 96-98] The most prominent are substitution at the backbone of the polymer or at the ortho position of the phenyl ring. Additional crosslinking can occur between the benzyl chloride residues and neighboring phenyl rings in the presence of a Lewis acid catalyst; also, cationic polymerization of unreacted vinyl groups has been observed. The extent of crosslinking can be reduced by avoiding impurities and using good swelling solvents.[78, 99] Elemental analyses of the various benzyl halide preparations are given in Table 3.

Concerning the SM-16 resin, Table 3 shows that the conversion from the chloride to the iodide is not quantitative; a second halide exchange reaction had no effect. The incomplete exchange could be due to vinyl chloride formation during the chloromethylation procedure or to limited reagent accessibility, since acetone is not a good resin swelling solvent. Vinyl groups are more prevalent in highly crosslinked resins due to incomplete polymerization. The resulting vinyl chlorides are less reactive toward further modifications than are the aromatic chloromethyl groups.[96]

Table 3. Elemental analyses of the functionalized macroreticular polystyrenes.[a]

	C	H	O	Cl	I	mmol/g[e]
Amberlite XE-305	91.25	7.67	1.64	------	------	------
PBnCl	75.56	6.65	2.16	16.30	------	4.60
PBnCl [b]	76.90	6.61	2.11	14.78	------	4.17
PBnI	54.47	4.62	1.48	0.00	39.24	3.09[f]
PBnI [b]	63.17	5.37	1.31	0.00	31.06	2.45[g]
SM-16 [c]	90.92	8.04	1.16	------	------	------
SBnCl [c]	79.64	7.62	3.65	9.54	------	2.69
SBnI [c]	73.51	6.98	3.34	2.08	13.89	0.59 (Cl)
						1.09 (I)
SBnI [c, d]	74.10	6.89	3.37	2.23	13.98	0.62 (Cl)
						1.06 (I)

[a] P = Amberlite backbone, S = SM-16 backbone, Bn = benzyl group. [b] Batch No. 2. [c] Single analysis, all other values are averages of duplicates. [d] A second halide exchange performed on the previous entry. [e] Calculated degree of halide incorporation. [f] Corresponds to 1 iodine per 1.8 styrene units. [g] Corresponds to 1 iodine per 2.6 styrene units.

Table 3 also shows that high benzyl chloride loadings were achieved in the Amberlite system. The chloride groups were completely displaced during the Amberlite benzyl iodide preparations. The halide exchanges were readily discernible by Fourier transform infrared (FTIR) spectroscopy in which the characteristic benzyl chloride signal at 1265 cm^{-1} was replaced by a benzyl iodide signal at 1155 cm^{-1}.

Electron microscopy x-ray analyses (SEM-EDS) of the Amberlite benzyl halides showed that the cross-sectional distributions of Cl and I were homogeneous. Similar results were observed by Belfer et al.[100] The distribution is reportedly dependent upon the chloromethylation method employed.[101]

Amberlite XE-305 was acknowledged as the better support since it exhibited a significant level of reactivity which should allow for the preparation of a resin with a high degree of model loading. The highly crosslinked Biobead SM-16 resin did not appear to be suitable for further study primarily because of its low halide exchange yield.

Diffusion in the Macroporous Network

Amberlite XE-305 was chosen as a support in part because of its intrinsically large average pore diameter. At 1400 Å, the macroreticular network would not be expected to impede the diffusion of reactants. The porous structure of polystyrene resins are known to change, however, upon thermal treatment.[102] A study was conducted to determine if the kinetics of the heterogeneous reaction system would be under the realm of diffusion or chemical reaction control.

Theoretical Considerations

Halász and coworkers report that the porous structure of the support will not be rate limiting if the pore size is greater than 2.5 times the random coil diameter of the infusing soluble species.[103, 104] The random coil diameter can be calculated from Eq. 5:[104]

$$d = 0.2457\ (Mw)^{0.5882} \qquad [5]$$

where d is the the random coil diameter in Å and Mw is the formula weight in

grams. The random coil diameter for syringyl alcohol calculated from Eq. 5 is 5.28 Å, a value which is significantly smaller than the 1400 Å pore diameter of the unmodified resin support. It appears, based on the above calculation, that a catastrophic collapse of the porous network would have to occur under pulping conditions in order for mass transport phenomena to become the rate limiting step.

Activation Energy

The activation energy for the hydrolysis of polymer-bound benzyl iodide (Eq. 6) was determined in order to confirm that diffusion of reactants into the functionalized resin would not be rate limiting under pulping conditions.

$$\text{PBnI} + \text{NaOH} \longrightarrow \text{PBnOH} + \text{NaI} \qquad [6]$$

A kinetic analysis was conducted with polymer-bound benzyl iodide at 130, 150 and 171 °C in 1M NaOH (Fig. 6). The extent of reaction was determined by elemental analysis (single determinations for iodine). The rate of iodide displacement was noticeably slow at the lower two temperatures, 130 and 150 °C. However, a significant rate increase was apparent at 171 °C. After 150 min, the displacement rate at 171 °C experienced a marked decline which suggests that the remaining unreacted iodide units reside in sterically hindered[105] or more inaccessible regions, such as the microgel phase, of the polymeric network.[69] An activation energy of 25.0 kcal/mol was determined from a pseudo first order kinetic application of the Arrhenius equation; a correlation coefficient (r^2) of 0.973 was observed. Analysis of

the product beads by FTIR gave a spectrum consistent with a polymer-bound benzyl alcohol.[106]

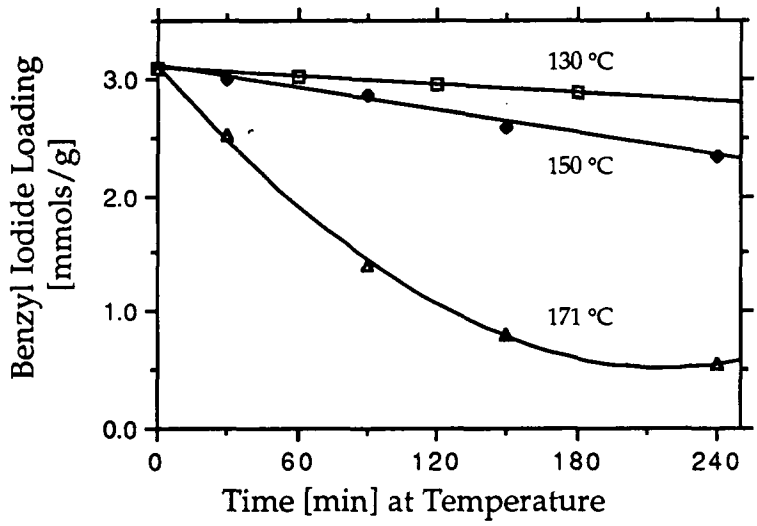
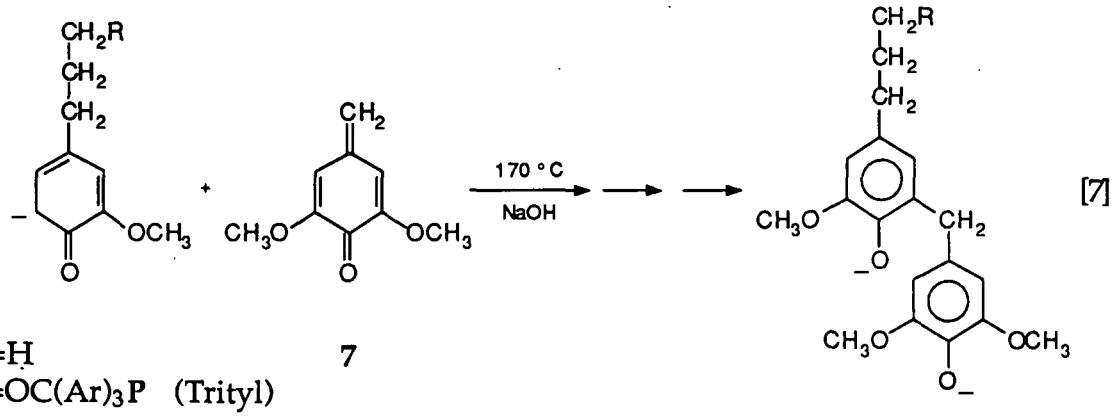


Figure 6. Polymer-bound benzyl iodide loading vs. time at the indicated temperatures.

Activation energies for chemically controlled bulk phase delignification under soda pulping conditions range from 20.5 to 35.1 kcal/mol for various wood species.[107-109] The activation energies for the initial phase pulping of eucalyptus, where diffusion is the rate limiting step,[110] range from 13.6 to 17.4 kcal/mol.[107] Therefore, the value found for the hydrolysis of polymer-bound benzyl iodide is consistent with chemical reaction control. Reaction rates in similar systems which employ Amberlite XE-305 as a support should also not be influenced by mass transport phenomena.

PREPARATION AND CHARACTERIZATION OF A POLYMER-SUPPORTED PHENOL

An equation which generalizes the primary condensation reaction between the C5 nucleophile of guaiacylpropane (**4** - **6**) and the soluble QM of syringyl alcohol (**7**) is presented below. The soluble-soluble reaction to be examined will be that of coupling **4** with **7**. The insoluble-soluble reaction counterpart involves condensing **5** or **6** with **7**. The relative yields of C5-Cα dimer (**8** - **10**) will be compared between the homo- and heterogeneous systems.



[7]

4, R=H
5, R=OC(Ar)$_3$P (Trityl)
6, R=OCH$_2$ArP (Benzyl, Bn)
P=polystyrene backbone [-CH$_2$-CH-]$_n$

7

8, R=H
9, R=OC(Ar)$_3$P
10, R=OCH$_2$ArP

The Trityl Ether Linked Model

Synthetic Approach

The preparation of polymer-supported, trityl ether linked, guaiacylpropanol (**5**) consisted of two primary operations. The first process involved a multistep

functionalization of the unmodified Amberlite XE-305 polystyrene resin (**1**) to a polymer-bound trityl chloride (**14**) as described by Farrall and Fréchet (Scheme 2).[111] The second phase consisted of coupling the lignin monomer, guaiacylpropanol (**15**), to the modified resin as described by Apfeld.[74] The trityl model is advantageous in that trityl chlorides react selectively with primary alcohols.[112] This obviates the need for protecting groups for the phenolic site when coupling the lignin model (**15**) to the modified resin. In addition, trityl ethers are readily hydrolyzed under mild acidic conditions[113] which allows for easy characterization and quantification of the bound model.[74]

Preparation of Polymer-supported Trityl Chloride

Bromination of the polystyrene resin occurs exclusively at the para site (Scheme 2).[114] The degree of bromination is a function of the amount of starting bromine which, in this case, was only 21% of the available phenyl nuclei.[111] Use of thallium acetate as a catalyst, vs. ferric chloride, results in a cleaner, more reactive substrate (**11**).[111] Elemental analysis was used to determine the degree of halide incorporation (Table 4).

The distribution of bromine was determined on a cross section of **11** by SEM-EDS. The highest concentration of bromine was found on the surface and outer-most region of the resin. The center of the resin appeared to be free of bromine as depicted in Figure 7. The gradient-type distribution exemplifies that the chemical reaction rate was faster than the rate of diffusion.[80, 115]

Scheme 2

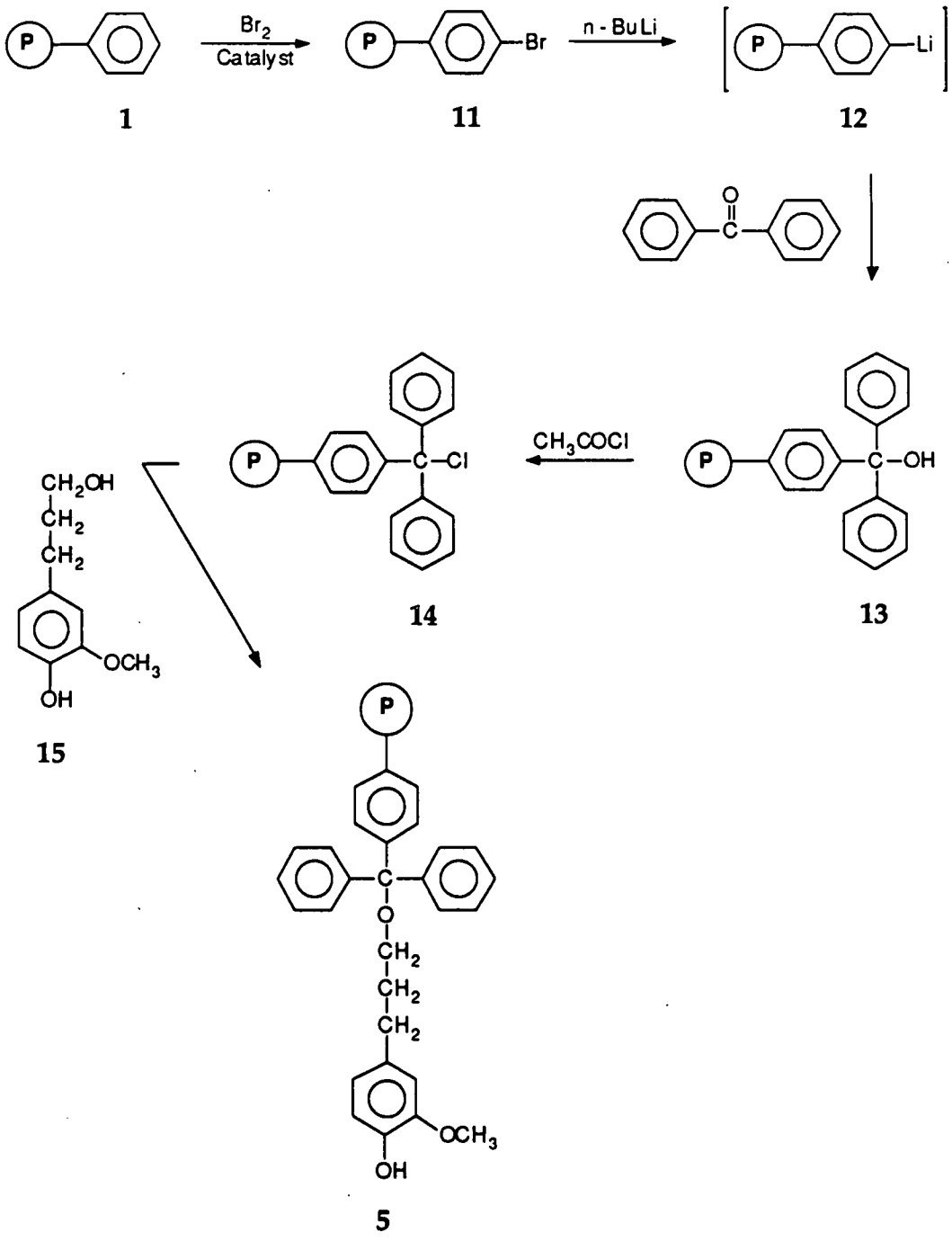

P
Br2
Catalyst
Br
n - BuLi
Li
1
11
12
O
C
CH3COCl
Cl
OH
14
13
CH2OH
CH2
CH2
OCH3
OH
15
5

Table 4. Elemental analyses of the functionalized polymeric products (**5, 11 - 14**).

Sample	C	H	O	Br	Cl	OMe	mmol/g[a]
11	80.57	6.79	1.77	11.17	----	----	1.39
13	87.82	7.45	3.33	0.73	----	----	----
14[b]	85.53	7.42	3.01	0.51	1.42	----	0.41
14[c]	85.81	7.18	2.30	0.44	1.83	----	0.53
5	89.67	7.61	2.68	----	----	0.69	0.22[d]

[a] Calculated degree of halide incorporation. All value are averages of duplicates. [b] Treated once with acetyl chloride. [c] Treated twice with acetyl chloride. [d] Calculated degree of lignin model loading.

The polymer-bound bromide was lithiated, giving heterogenous intermediate **12**, by treatment with an excess of n-butyllithium. The lithiated intermediate was not isolated due an acute sensitivity to air.[116] Quantitative conversions to the lithiated derivative have generally been observed for brominated macroreticular resins.[111] The lithiated resin can also be directly produced from unmodified

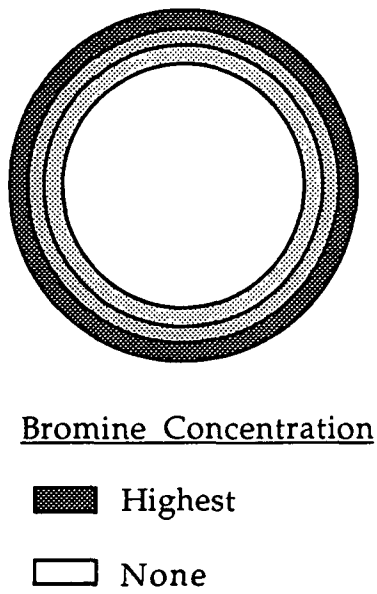


Figure 7. Cross-sectional bromine distribution of brominated polystyrene **11**.

polystyrene by treatment with n-butyllithium and N,N,N',N'-tetramethylethylenediamine.[117] This method is not, for the intended synthetic applications, preferable to the two-step bromination-lithiation sequence, since direct lithiation yields a meta-para reaction site ratio of 2:1.[118]

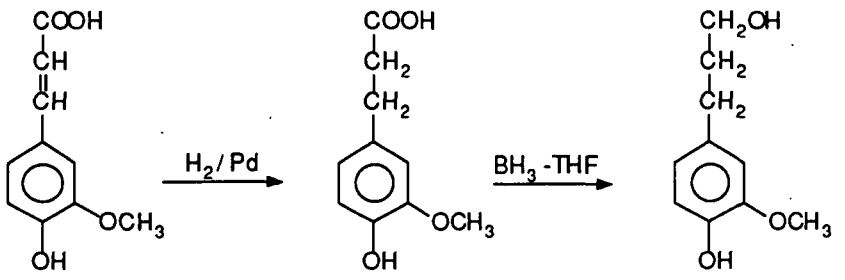
An immediate treatment of lithiated resin **12** with benzophenone in tetrahydrofuran (THF) resulted in the formation of trityl alcohol **13**. The polymer-bound trityl alcohol was then converted to the corresponding trityl chloride (**14**) by reaction with acetyl chloride. A low yield of chloride, 45% based on the bromine content of resin **11**, was observed. A second treatment of **13** with acetyl chloride resulted in a modest increase (0.12 mmol/g) in the chloride content (Table 4). The conversion of trityl alcohol to trityl chloride is typically quantitative.[119] The low overall yield of trityl chloride probably reflects only limited success in the coupling of benzophenone with lithiated intermediate **12**. The low level of trityl alcohol **13** was confirmed by the FTIR spectrum which showed a weak hydroxyl signal. A procedure for preparing highly loaded (2.5 mmol/g) polymer-supported trityl chloride has since been reported.[120]

Preparation of Polymer-supported Trityl Ether Linked Guaiacylpropanol

Guaiacylpropanol (**15**), 3-(3'-methoxy-4'-hydroxyphenyl)propan-1-ol, was prepared from ferulic acid (**16**) in a two-step procedure (Scheme 3).[74] The initial reaction involved the catalytic hydrogenation of the alkene double bond on **16**. The

carboxylic acid group on the resulting dihydroferulic acid (**17**) was then reduced to a primary alcohol by reaction with a borane-THF complex.

Scheme 3



16 **17** **15**

Guaiacylpropanol was coupled to the trityl chloride (**14**) by slurrying the two reactants in a benzene/pyridine solvent mixture for several days. Benzene was added as a cosolvent to improve the swelling of the resin.[121] A loading of 0.22 mmol/g (Table 4) was determined for **5** by methoxyl analysis. Reproducible loading values could not be obtained by hydrolyzing the trityl ether bond with trifluoroacetic acid.[74, 113]

Stability of the Trityl Ether Linkage Under Alkaline Pulping Conditions

Trityl ethers are reportedly stabile under high temperature alkaline conditions (pH > 12 and 150 °C).[122a] Indeed, previous results showed that the trityl ether linkage of tritylated guaiacylpropanol, the soluble analog of **5**, was stable under kraft conditions (2 hr at 150 °C in 0.11M NaOH/0.021M NaSH with 29% p-dioxane added to ensure solubility).[74] The same degree of stability was not, however, observed

with the heterogeneous model (**5**, referred to as sample A). Approximately 25% of the bound guaiacylpropanol was released into solution when treated under kraft conditions (Table 5).[74] The loss of compound **15** appeared to occur during the first hour at temperature after which the level retained on the resin remained constant. Based on these results, it was determined that a stable heterogeneous substrate could be obtained by "conditioning" the model for one hour under high temperature alkaline conditions.

The stability of the trityl ether linkage on freshly prepared **5** (sample B) was determined under both soda (1M NaOH) and kraft conditions. As shown in Table 5, both media resulted in significant losses (78 and 75%, respectively) of bound model. Examination of the data in Table 5 showed that the fraction of cleaved ether bonds (a) is fairly high, (b) levels off with long reaction times, (c) is not very sensitive to the presence of NaSH, (d) is temperature dependent, and (e) differs significantly with the polymer substrate employed.

Reasons for the stability differences are not well understood. Both sample A and B had similar loading values, 0.26 and 0.22 mmol/g, but differed in the solvent used in the coupling of guaiacylpropanol to the polymer; sample A used pyridine, while sample B used a mixture of pyridine and benzene. The method for determining the level of released guaiacylpropanol (**15**) was also different. For sample A, the level of **15** in solution was measured by gas-liquid chromatography (GLC).[74] For

sample B, the level of released **15** was calculated by difference based on the methoxyl loading value of reacted heterogeneous model **5**.

Table 5. Yields of guaiacylpropanol (**15**) liberated from polymer-supported guaiacylpropanol **5**.

Time	% **15** from Prep. A[a, 74]		% **15** from Prep. B[b]	
(min)	Kraft 135 °C	Kraft 150 °C	Kraft 147 °C	Soda 147 °C
15	4	14		
30	8	18		
45		21		
60	12	25	41	41
90	15	23		
120	15	24		59
150			75	
180				68
240	17	25	75	78

[a] Kraft: 0.11M NaOH, 0.021M NaSH; analysis by GLC of released **15**. [b] Kraft conditions as above; soda: 1M NaOH; analysis by methoxyl determination of reacted resin.

The observed instability of the trityl ether linkage may be due to the heterogeneous nature of the labile bond. As part of a polystyrene network, the trityl groups may be intrinsically strained, thereby forming relatively weak trityl ether bonds. The weak ethers may be more susceptible to cleavage than the unstrained soluble trityl ethers. The portion of bound trityl ethers that are stable may be in a less strained environment and thus are able to maintain a degree of alkali stability similar to that of their soluble analogs.[74]

Another explanation could be that there are a variable number (depending on the preparation) of bound models in environments conducive to heterolysis

reactions. For example, regions which are exposed to the alkaline pulping liquor may experience model-polymer bond breakage, presumably via an S_N1 type mechanism, while other regimes, having principally an impenetrable "organic" environment, are stable. It may be possible then that the "soluble" models were not really soluble, but formed impenetrable micelles, which protected the trityl bonds from cleavage reactions and provided the illusion that the molecules were inherently stable.[121]

Lending support to these arguments, different degrees of model loading were obtained depending upon the solvent used in the coupling reactions leading to a polymer-bound cellulose model.[75, 123] Also, with the cellulose model, the methods used to determine model loadings did not always agree. The different solvents used during the preparation of the model may result in different degrees of polymer swelling and thus different degrees of polymer reaction.[121]

The above results show that the linkage between the model and the polymer, a trityl ether type, does not exhibit an adequate level of stability in aqueous alkali at 150 °C. This lack of stability prevents heterogeneous trityl ether linked models from being useful substrates in the study of pulping reactions. The trityl linked models may, however, have value for studying heterogeneity effects under less severe conditions, such as exist in pulp bleaching or biodegradative reactions of lignin.[121]

The Benzyl Ether Linked Model

Synthetic Approach

A pulping stable model-to-polymer linkage was sought once it was demonstrated that the heterogeneous trityl ether linkage was readily cleaved under simulated alkaline pulping conditions. A benzyl ether model-to-polymer bond, which linked a carbohydrate model to a polystyrene support, demonstrated a high degree of stability under harsher alkaline conditions, 170 °C in 1M NaOH for several days.[75] The benzyl ether linkage thus appeared to be a viable alternative to the unstable trityl ether linkage.

Iodomethylated polystyrene (**3**) was employed as the functionalized resin to which the lignin monomer guaiacylpropanol (**15**) was to be attached. As previously discussed, the preparation of the iodomethylated resin, requiring only two steps (Scheme 1), was much less involved than that of the trityl chloride (**14**) and did not involve any sensitive intermediates, e.g. lithiated polystyrene (**12**). The iodomethylated resin, unlike the trityl chloride, possessed a high halide loading which was distributed evenly (SEM-EDS) over the surface and interior regions of the resin. A high and relatively homogeneous halide content increases the probability of a high and more uniform model loading. The resulting heterogeneous substrate should, with a higher density of model, more accurately resemble lignin than the trityl ether linked moiety where the distribution of model was sparse and located only on the outer regions of the support.

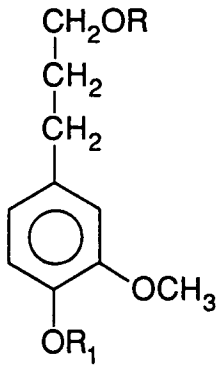
Coupling of guaiacylpropanol to the heterogeneous benzyl halide was not, however, as simple as in the trityl synthesis. This subject will be elaborated on in the following text.

Protected Lignin Models

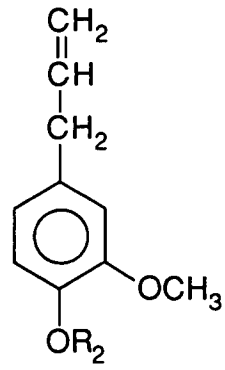
Preliminary work with guaiacylpropanol (**15**) defined the conditions required to generate model-to-polymer benzyl ether linkages. Selectivity for reaction at a primary alcohol group,[112] as was previously encountered during the preparation of the trityl-linked model, was not observed in the benzyl case. Treatment of compound **15** in dimethylsulfoxide with sodium hydride (NaH) followed by benzyl bromide did not give the anticipated propyloxybenzyl product **18**; rather benzylation occurred principally on the phenolic hydroxyl group (**19**).[124]

This result suggested other possible protecting group methods. For example, guaiacylpropanol (**15**) was reportedly treated with p-methoxybenzyl iodide[122b, 125] to give **20**; the latter was then benzylated, affording **21**.[124] Attempts to specifically remove the p-methoxybenzyl group by treatment with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) led to a complicated product mixture, rather than pure **18**. Apparently, the DDQ also oxidized the electron-rich ring of the model.

Similarly, methoxyethoxymethyl (MEM) ether was investigated as a potential protecting group. Selective removal with trifluoroacetic acid made the MEM ether attractive.[126] The MEM protected model **22** was prepared by first synthesizing the



15, R=H, R_1=H
18, R=Bn, R_1=H
19, R=H, R_1=Bn
20, R=H, R_1=p-BnOMe
21, R=Bn, R_1=p-BnOMe
22, R=H, R_1=MEM
25, R=H, R_1=allyl
26, R=Bn, R_1=allyl



23, R_2=H
24, R_2=MEM

MEM ether of eugenol (**23**) and then hydrating **24** with disiamylborane/hydrogen peroxide.[127] Difficulties were encountered, however, in benzylating the protected model **22** under the reflux conditions suggested in the literature.[126] Analysis of the product mixture by gas-liquid chromatography/mass spectroscopy (GC/MS) revealed that the MEM group was not completely stable. Instability was also encountered at reduced temperatures (40-50 °C) during an attempted coupling reaction in THF with iodomethylated polystyrene (**3**). Milder conditions (room temperature) were not explored.

Bovee successfully used allyl groups to protect several hydroxyls on a di-saccharide that was subsequently attached to a polystyrene support through a benzyl ether linkage.[75] Guaiacylpropanol was readily protected at the phenolic site with an

equimolar amount of NaH and an excess of allyl bromide to give **25**. The allyl-protected model (**25**) was readily benzylated yielding **26**. The allyl group was quantitatively removed from **26** by isomerization to a prop-1-enol with tris(triphenylphosphine)rhodium(I) chloride (TTPPR) and 1,4-diazabicyclo[2.2.2]octane (Dabco), followed by acid catalyzed hydrolysis to give **18**.[128] Complete isomerization of the phenolic allyl group required over 24 hr at reflux, compared to 6 hr for primary or secondary hydroxyls.[128-130] Allyl isomerization via potassium t-butoxide in DMSO was unsuccessful.[131] Cleavage of the prop-1-enol ethers by hydrochloric acid (HCl) in acetone was also sluggish requiring reflux conditions. Triphenylphosphine and its oxide, which were observed in the isomerization product mixture, should be easily removed in the heterogeneous case by simply washing the resin.

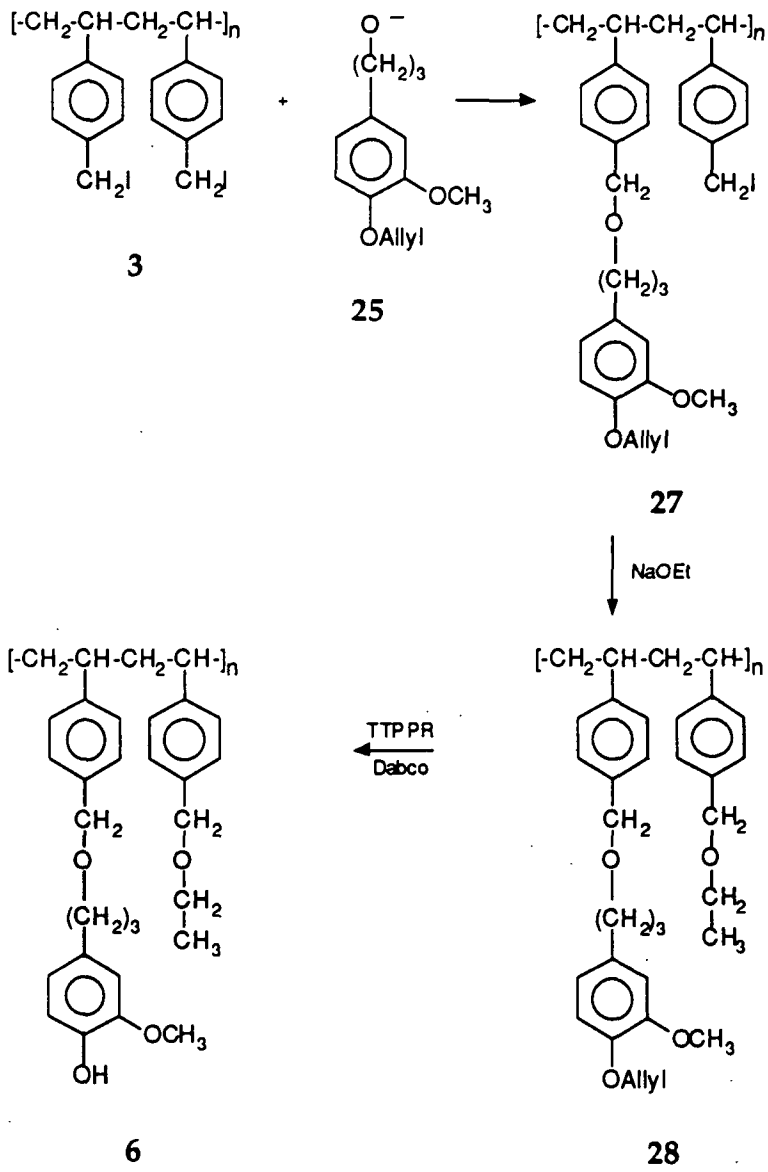
Thus, the allyl group appeared to possess the required protecting group qualities: selective phenolic protection, stability during benzylation, and high yield selective deprotection in the presence of a benzyl ether.

Preparation of Polymer-Supported Guaiacylpropanol

Initial attempts at coupling allyl-protected guaiacylpropanol (**25**) to the polymer-bound benzyl iodide (**3**) were performed in 25% benzene/N,N-dimethylformamide (DMF), using NaH to deprotonate the primary alcohol (Scheme 4). Analysis of the resulting product (**27**) by FTIR showed strong hydroxyl and carbonyl absorbances which indicated that the DMF had sorbed onto the resin. Extended Soxhlet extraction of the resin did not remove the impurities. The coupling yield

was presumably low since the FTIR spectrum did not show evidence of the allyl group.

Scheme 4



Tetrahydrofuran, also a good swelling solvent for the resin, replaced DMF as the coupling solvent in a second attempt to bind model to the polymer. The FTIR spectrum of the coupled product (**27**) did not show any evidence of solvent absorption. An analysis of the liquor from the coupling reaction revealed starting material **25**, thus confirming that the allyl group was stable under the prescribed reaction conditions.

The loading of the coupled material was apparently much higher than in the DMF case; infrared signals at 997 and 926 cm^{-1} (C=C-H bend) attested to the presence of the allyl group. The benzyl iodide FTIR signal was still evident, however, indicating that the displacement was not quantitative. An estimate of the model loading was determined by the weight gain of the polymer following the coupling reaction;[74] this gravimetric analysis gave 1.57 mmol of model per gram of resin.

The second step in preparing the heterogeneous model involved etherification of the remaining benzyl iodide groups. The residual benzyl iodide units (on **27**) were converted to nonreactive benzyl ethoxide groups (**28**) by treatment with sodium ethoxide in ethanol. An FTIR spectrum of the ethoxide treated resin showed that the initial benzyl iodide signal had been replaced by the corresponding benzyl ethoxide signal at 1097 cm^{-1}. Model experiments under the above reaction conditions confirmed that the allyl protecting group was stable toward sodium ethoxide.

The final step in preparing the model involved removal of the allyl group with the TTPPR/Dabco/acid hydrolysis method to generate the free phenol **6**. The

FTIR spectrum of the deprotected material (**6**) showed a strong hydroxyl absorbance indicating that some free phenol had been produced. The allyl signals were still evident, however, suggesting that the deprotection was incomplete. Two additional deprotection sequences were needed to remove the FTIR allyl absorbances.

A high resolution ^{13}C-NMR (CMR) technique[132] was also used to characterize selected resin samples (Fig. 8). The spectra, obtained using conventional methods by simply suspending the resin in $CDCl_3$, suffer from band broadening due to the heterogeneous nature of the substrate. In general, the spectra for the polymer-supported appendages were consistent with comparable soluble compounds.

The CMR spectrum of the iodomethylated polystyrene resin **3** (Fig. 8A) exhibited signals that were consistent with a polystyrene backbone.[132-134] The signal for the heterogeneous benzyl iodide carbon, which for the soluble analog (α-iodo-toluene) comes at 5.9 ppm,[135] was not readily apparent. The signal for the precursor benzyl chloride (**2**) carbon at 46 ppm was also not observed.[132-134] This latter result confirms the elemental analysis of iodide **3** (Table 3) in which no chlorine was detected.

Treatment of **3** with sodium ethoxide provided the corresponding ethoxy-methylpolystyrene where the ethyl and benzyl signals were quite pronounced (Fig. 8B). It appears from this spectrum, and the ones which follow, that those carbons furthest removed from the polymer backbone display the strongest signal intensities. This phenomenon is related to differences in carbon relaxation times between

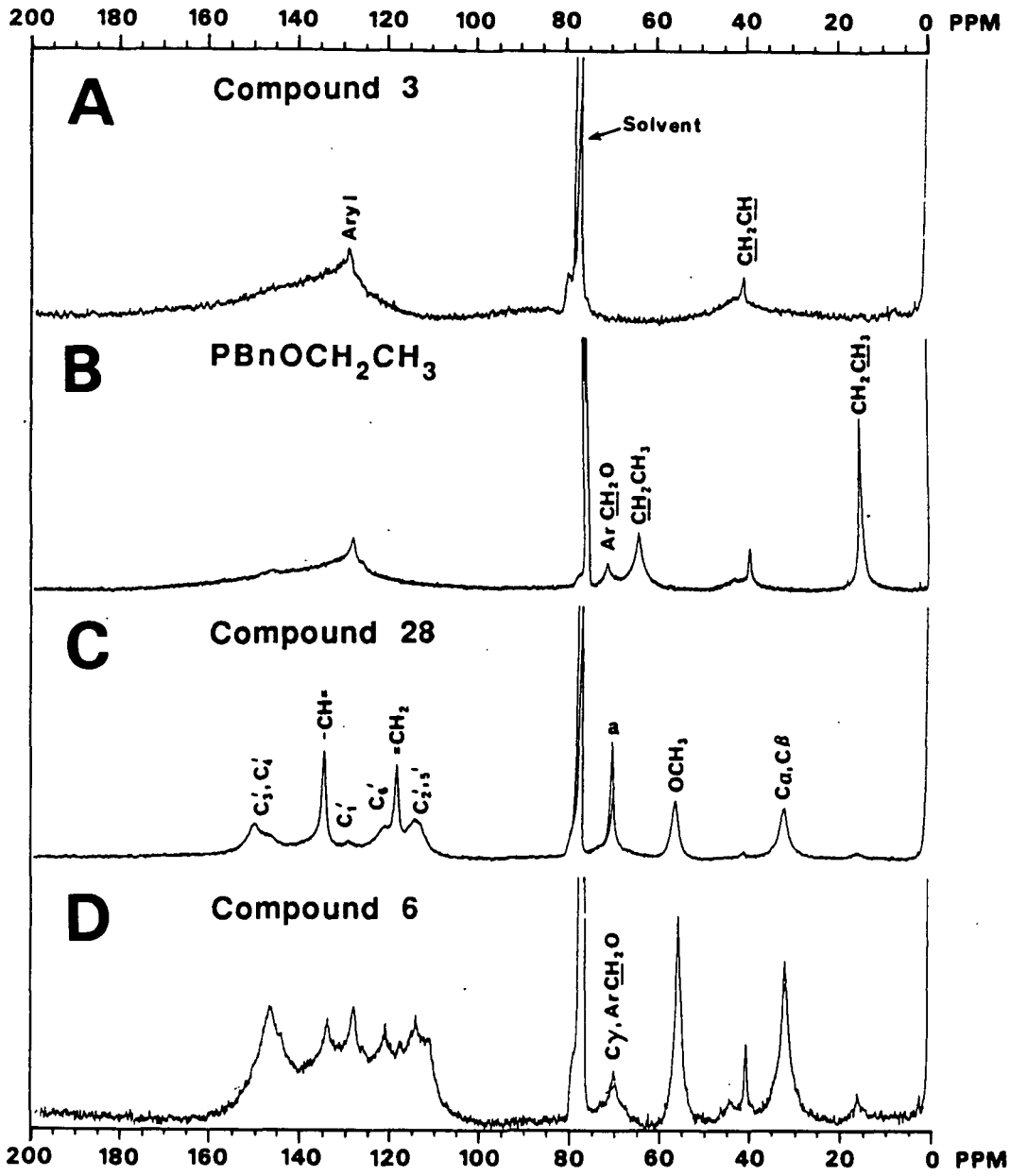


Figure 8. The ^{13}C-NMR spectra of selected resin samples; the area between 78-80 ppm represents solvent signals ($CDCl_3$). Signal "a" appears to be a combination of carbon types as described in the text.

the more motionally inhibited nuclei close to the heterogeneous support and those with more rotational freedom at the unbound end of the attached molecule.[132]

The CMR spectrum of polymer **28** (Fig. 8C) clearly showed the 4-O-allyl-guaiacylpropanol appendage. The allyl protecting group, which is the functional unit furthest removed from the polymer backbone, showed strong signals at 70, 117, and 135 ppm. The propyl carbons were indicated by signals at 30-35 and 70 ppm. The presence of an oxygenated aromatic ring in the resin was demonstrated by the methoxyl signal (56 ppm), together with the high field (135-150 ppm) signals for aryl-oxygen carbons and the low field (110-115 ppm) signal for aryl carbons which are ortho to aryl-oxygen substrates.

Finally, the spectrum of resin **6** (Fig. 8D), which exhibited a greater signal intensity than the other spectra, clearly showed that most of the allyl groups have been removed. Residual allyl signals were detected, however, at the resonances cited above. The oxygenated aryl ring, the methoxyl and the Cα/Cβ propyl carbons were again readily distinguished. The signals associated with the oxygenated methylenes of Cγ and the benzyl unit cannot be clearly assigned; they appeared to be either part of the 70 ppm signal or overlapped with the strong solvent signal at 78-80 ppm. The relatively low signal intensity for the ethoxy groups (15 and 66 ppm) in resins **28** and **6** indicate that most of the polymer-bound benzyl iodide units were consumed by reaction with guaiacylpropanol. A fourth deprotection sequence was not

attempted, since the remaining allyl groups appeared, by their inactivity, to reside in inaccessible regions of the resin.

Table 6 summarizes the elemental analysis data of each intermediate and the final product. The low iodine content of the initial coupling product (**27**) provided more evidence that model-resin coupling was extensive. The high conversion suggested that the distribution of the model was essentially that of the initial benzyl iodide. Phosphorus was detected in product **6**, indicating that a small quantity of triphenylphosphine residues had sorbed to the polymer. The phosphine residue, if covalently bonded to the resin, should be inert toward the subsequent condensation reactions.

Table 6. Elemental analyses (duplicates) of the compounds isolated during the preparation of the heterogeneous lignin model.

Substrate	C	H	O	I	P	I loading (mmol/g)
27	76.43	7.28	9.50	6.15	---	0.48
28	79.36	7.65	11.18	1.41	---	0.11
6	78.09	7.42	12.47	0.11	0.29	<0.01

Model Loading Determination

Gravimetric and elemental analysis data, along with the FTIR and ^{13}C-NMR spectra, showed that a significant quantity of model had been covalently bound to the polymer via a benzyl ether linkage. A method to quantify the amount of material on the resin was sought.

Methoxyl analyses of the trityl-linked lignin models gave quantitative results.[74] The methoxyl method was not, however, applicable to the present benzyl-linked model (**6**) since ethoxide groups, which were added to destroy the excess reactive benzyl iodide groups, are known to interfere with the determination.[136] Initially, a propyl group was investigated as an etherification reagent. Subsequent analyses with polymer-bound propoxide (no model was attached) gave positive methoxyl results; the same was found with an allyl etherified resin.

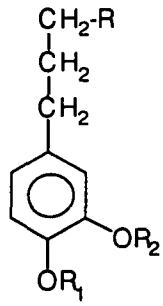
Another approach to quantification was to derivatize the polymer-bound phenol with a functional group that had an easily analyzable element. This approach was taken with heterogeneous model **6** using pentafluoropropionic anhydride and a pyridine catalyst.[137] The resulting pentafluoropropionate was found to be unstable over time giving inconsistent results. The heterogeneous derivatization, unlike that of a soluble phenol, was shown by FTIR to be incomplete.

Methods for quantitatively cleaving the heterogeneous benzyl ether bond, in order to isolate and analyze the amount of guaiacylpropanol liberated, were investigated. Benzyl ethers are readily cleaved by catalytic hydrogenation.[122c] This method could not, however, be implemented due to the two insoluble phases.[138] Several other reagents were tested without success. These systems included boron trifluoride with ethanethiol,[139] acetolysis,[75] and anhydrous ferric chloride with acetic anhydride.[140]

A neutral compound, iodotrimethylsilane (ITS), proved to be an effective reagent for severing heterogeneous benzyl ether linkages. Iodotrimethylsilane reportedly cleaves (soluble) benzyl ether bonds quantitatively under mild reaction conditions.[141, 142] Tests with benzylated allylguaiacylpropanol (**26**) showed complete benzyl group removal in 20 min at room temperature. The allyl group was also cleaved but at a slower rate. Reaction of heterogeneous model **6** with ITS, followed by acetylation of the released product, yielded **29**; the latter could be quantified by GLC using an internal standard. A similar reagent system, chlorotrimethylsilane in the presence of phenol, has been used effectively on polymer-bound substrates.[143]

Several minor compounds (**30 - 32**) were detected in the product mixture. Combined, they accounted for less than 5% of the amount of guaiacylpropanol present. Iodo compound **30** could result from two routes. The most likely prospect is that excess ITS converts the silated propyl alcohol function to the iodide after the model has been cleaved.[142, 144] The other possibility is that the model is cleaved as the iodide rather than as the alcohol. The literature reports that for soluble models the cleavage is 100% for the benzyl iodide, giving the free alcohol.[142] This may not be the case in the heterogeneous system.

The appearance of compound **31** indicated that a small amount of methyl aryl ether cleavage had occurred. Methyl ether cleavage during ITS treatment is known to be slow relative to that of the benzyl ethers and often requires harsher conditions.[142, 145] Compound **32**, which is observed in trace quantities, is believed to



29, R=OAc, R_1=Ac, R_2=CH_3
30, R=I, R_1=Ac, R_2=CH_3
31, R=OAc, R_1=Ac, R_2=Ac
32, R=OAc, R_1=n-propyl, R_2=CH_3

result from the reduction of residual allyl groups during the course of the synthesis. The propoxy group on **32** effectively prohibits the model from undergoing condensation reactions.

The ITS procedure for quantifying the model on the resin is simple and reproducible, giving a loading of 1.29 ± 0.04 mmol/g. Quantitative results were, however, not obtained. The FTIR spectrum of ITS treated resin showed residual model; a significant benzyl iodide signal indicated, however, that a majority of the model had been displaced. In some cases, a broad signal attributable to a silyl ether was observed; the signal could be removed with concomitant generation of the corresponding alcohol by treatment with citric acid in methanol.[146] The inability to quantitatively cleave bound substrates from the resin has been cited as a disadvantage in working with supported reagents.[147]

A product of the ITS reaction, as shown by FTIR, is polymer-bound benzyl iodide. A microscopic x-ray analysis (SEM-EDS) of the ITS treated resin showed that iodine was present in the innermost regions of the bead at a uniform level, — no gradient from the outer edge of the bead was observed. The iodine distribution indicates that the macroporous regions of the resin are accessible to the ITS during the 30 min reaction period.

The results of the ITS procedure suggest that not all of the bound model is accessible. The inaccessible model is presumably trapped within the microgel region of the resin. The model inaccessible to ITS would, most likely, be inaccessible to pulping liquors. Therefore, the loading value determined by the ITS method represents the amount of accessible model on the polymer support.

Stability of the Heterogeneous Model Under Alkaline Pulping Conditions

The stability of the benzyl ether linkage on the heterogeneous lignin model (**6**) was examined by cooking the resin in 1M NaOH for up to six hours at 170 °C. The iodotrimethylsilane (ITS) method was used to determine the amount of guaiacylpropanol (**15**) remaining on the resin after it was washed and dried. The reaction liquor was also analyzed for guaiacylpropanol. Figure 9 shows the results of the high temperature alkali treatments.

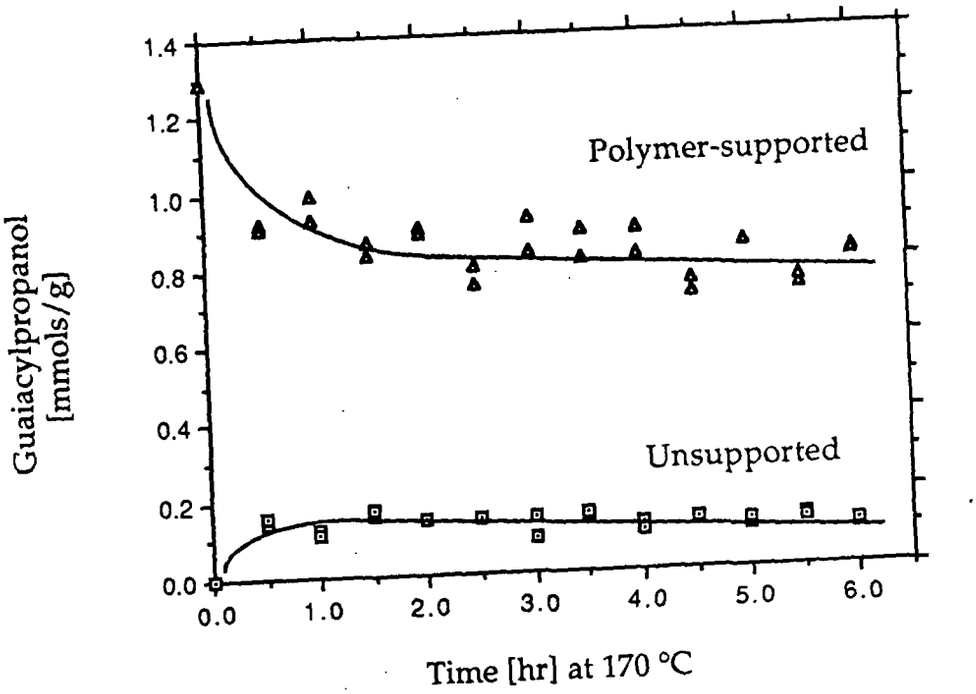
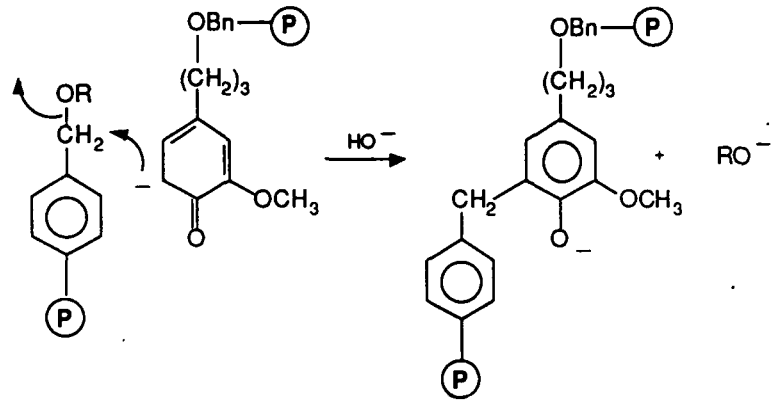


Figure 9. Stability of the heterogeneous benzyl ether linkage in 1M NaOH at 170 °C.

The low level (10%) of guaiacylpropanol found in solution remained relatively constant after 30 min at 170 °C. The resin, however, appeared to lose a significant amount of guaiacylpropanol during the first 90 min at temperature, after which the level of model remaining on the resin remained relatively stable. At the conclusion of the stability trial, the model loss was 40% based on the ITS analysis of the resin.

Several hypotheses may explain the loss of model from the resin. The first is depicted in Eq. 8. Due to a high loading level, and thus close proximity, some ionized model may react with a neighboring benzylic carbon and displace a guaiacylpropanol unit or ethanol. Low levels of ethanol (ca. 0.03 mmol/g) were detected in the reaction liquor. Intrapolymeric reactions have been observed for other

systems.[148-152] Crosslinked intrapolymeric units, as shown in Eq. 8, are difficult to detect by ^{13}C-NMR, thus eliminating this technique as a method to further confirm the interunit displacement hypothesis.[132]



R = model or CH_2CH_3

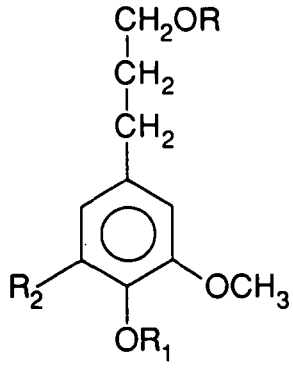
A second possibility is that a portion of the guaiacylpropanol is sorbed to the resin and not covalently bonded. Low levels of guaiacylpropanol (0.04 mmol/g) were observed in solution after the resin had been soaked in THF for 83 hr. A similar amount (0.03 mmol/g) was observed after 45 min in acetonitrile. At the higher temperatures used in the pulping trial, the morphology of the resin may change, freeing some internally absorbed guaiacylpropanol.

A change in resin morphology associated with high temperatures could also (a) release model into solution to relieve some internal stress and (b) collapse the resin in such a way that bound model is trapped in regions which, upon cooling, are inaccessible to the ITS reagent. In other words, the model was still attached to the polymer at roughly the same level as before heating, but the ITS loading technique

fails to recognize the inaccessible guaiacylpropanol. This would explain the non-quantitative mass balance, which ranges initially from 85% down to 65%, observed over the course of the extended soda cook.

The initial instability of the polymer-bound model necessitated that it be "conditioned" in alkali at 170 °C (90 min) before undergoing any further reactions. A new loading value of 0.81 ± 0.04 mmol/g was determined for the conditioned reactant. The FTIR spectrum of the conditioned model remained similar to that of its unconditioned precursor. The elemental analysis (C, 80.71; H, 7.28; O, 11.64 %) varied only slightly from that of the unconditioned material (see Table 6). Subsequent experimentation confirmed the stability of the conditioned model.

A new minor compound (**33**), amounting to less than 2% of the observed guaiacylpropanol, was identified by GC/MS in the acetylated ITS product solution of the conditioned resin. Compound **33**, which has an allyl group at the C5 position on the aromatic ring, is most likely derived from polymer-supported **34**. Compound **34**, in turn, appeared to result from a Claisen rearrangement[94b] of the allyl group from the phenolic oxygen of structure **35** to C5 under high temperature alkaline conditions. The observation of **33** confirmed the results of the ^{13}C-NMR spectrum (Fig. 8D) which showed that the allyl groups were not completely removed during the polymer model synthesis. Any residual **34** structures on the polymer should be inactive toward condensation reactions since the otherwise reactive C5 position is blocked by an alkali stable allyl group.



33, R=Ac, R_1=Ac, R_2=Allyl
34, R=BnP, R_1=H, R_2=Allyl
35, R=BnP, R_1=Allyl, R_2=H

PREPARATION AND CHARACTERIZATION OF A POLYMER-SUPPORTED QUINONE METHIDE

Initial Model Design

The primary objective in this phase of the research was to prepare a well defined QM immobilized on a heterogeneous support. Such a substrate could be utilized to compare the effectiveness of industrially important pulping additives (e.g. the hydrosulfide ion or anthrahydroquinone) at inhibiting condensation on insoluble relative to soluble quinone methides.

The initial synthetic route envisioned for the preparation of the supported QM is illustrated in Scheme 5. As depicted, the heterogeneous QM (**39**) was to be equipped with a six carbon "spacer" side chain. Several literature reports have shown that bound reactants are more active, in part due to steric considerations,

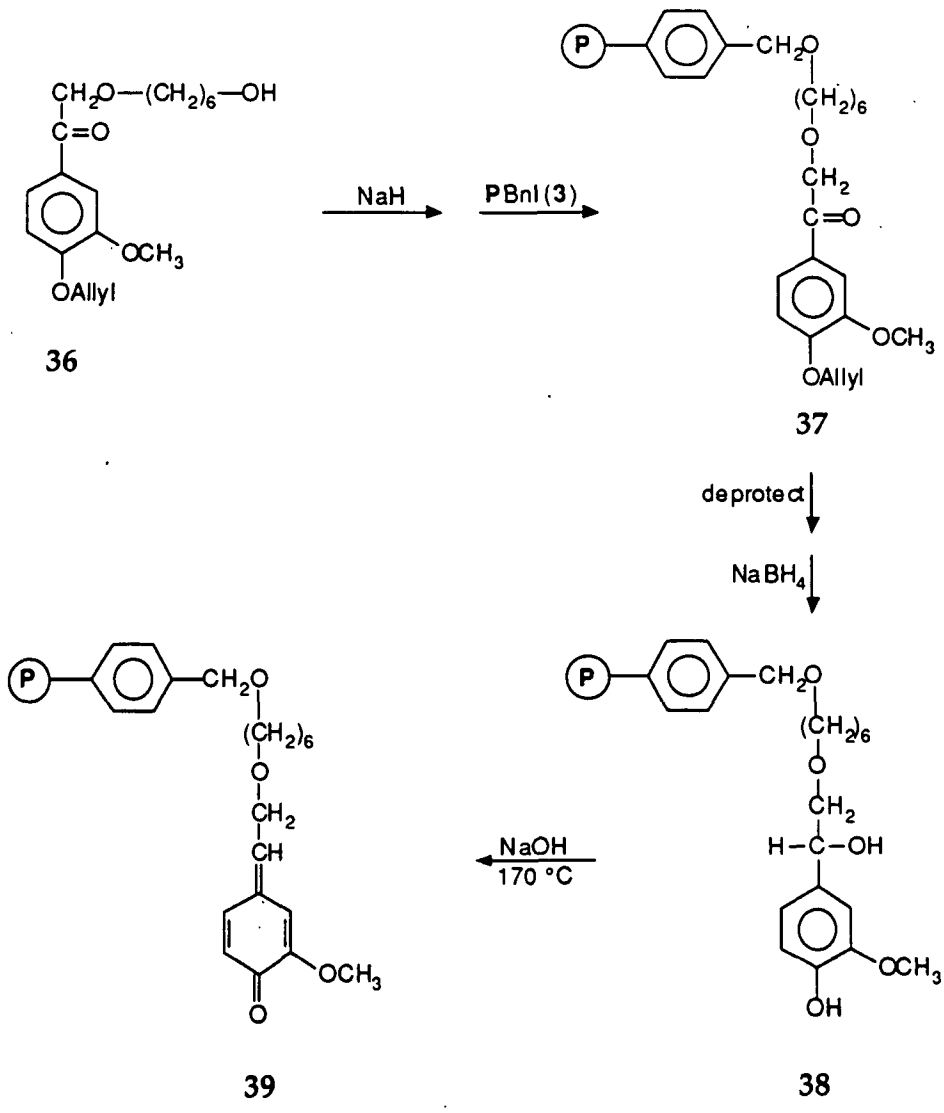
when placed further away from the polymer backbone.[153-157] Recall that insoluble polymeric phenol **6** essentially had a three carbon spacer.

Apfeld[74] worked with a trityl ether linked model somewhat similar to **38**. His model contained a three carbon (beyond Cβ) spacer side chain. Subsequent tests under simulated pulping conditions showed that the ionized α-hydroxyl group could cyclize forming a stable six-membered ring thus effectively displacing the model off of the supporting polymer. Apfeld's results justified using a larger spacer side chain. Chances of model displacement via cyclization become much less with the longer spacer since the driving force would be the formation of an unstable ten-membered ring.[94d]

Another advantage of the proposed model is that the α-hydroxyl group (**38**) can be prepared from the attached ketone (**37**) by a sodium borohydride reduction;[138, 157] only one protecting group, at the phenolic site, would then be required when coupling model **36** to the polymer. The conditions for utilizing an allyl protecting group methodology were worked-out in the previous insoluble phenol system.

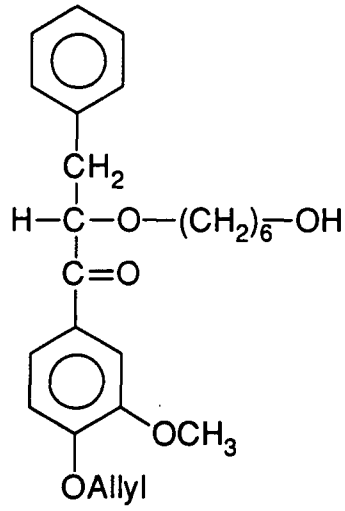
Solution phase benzylation tests were conducted with soluble model **36** before attempting to attach it to the iodomethylated polystyrene support (**3**). Benzylation did occur but not at the desired site. Apparently the strongly electron withdrawing α-carbonyl group of **36** made the neighboring Cβ protons more acidic than the primary hydroxyl group at the end of the six carbon side chain. Benzylation therefore

Scheme 5

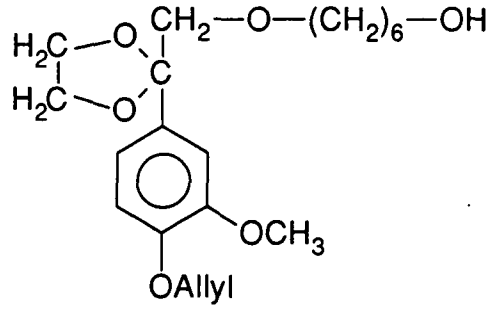


occurred at Cβ (**40**) where the negative charge resided. The carbonyl group was thus protected by an electron donating 1,3-dioxolane structure (**41**) in order to lessen the acidity of the Cβ protons.[94c, 158] Unfortunately, attempts at benzylating **41** were unsuccessful; the resulting anion (**41**$^-$) was relatively insoluble in THF, the solvent that had performed well when coupling other models to the modified resin support.[75]

The addition of a cosolvent (p-dioxane) and raising the temperature (40 °C) did not promote benzylation.

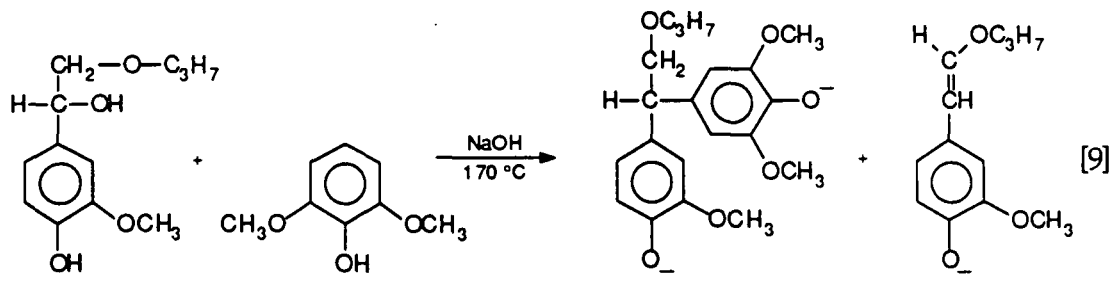


40



41

The soluble analog (**42**) of proposed heterogeneous appendage **38** was concurrently prepared and reacted under high temperature alkaline conditions with a three-fold excess of syringol (**43**) to discern whether condensation would occur at a sufficient rate (Eq. 9). Syringol, which is not a common pulping by-product, was chosen as the soluble nucleophile because of its potential for reaction and inability to self-condense. The consumption of starting material was rapid; only a trace of **42** was observed after one hour at 170 °C in 0.050M NaOH. As shown in Eq. 9, two product types were detected in the reaction liquor. The major species (71%) was the C1-Cα dimer (**44**). Both the cis and trans vinyl ethers (**45**, trans shown) were detected in lesser amounts (29% total).



42 43 44 45 [9]

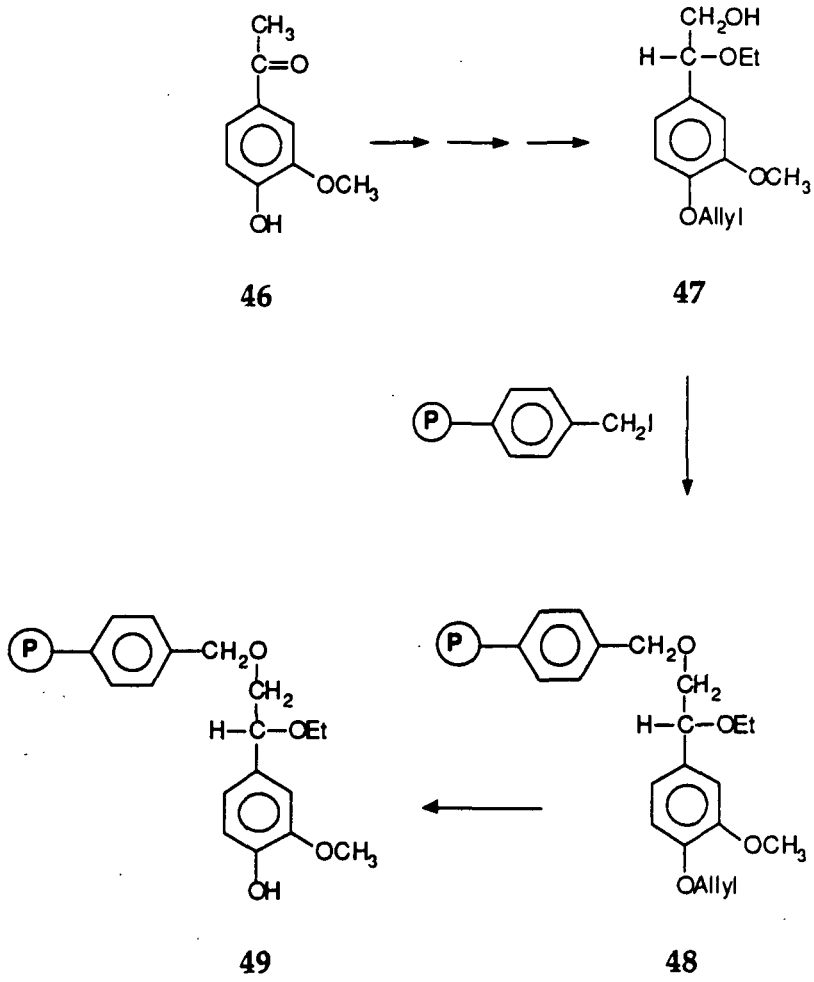
No dimer (C5-Cα) was detected under harsher conditions (1M NaOH) when an equimolar amount of creosol (2-methoxy-4-methylphenol) replaced syringol as the ligninlike nucleophile. Several studies have demonstrated that C5 nucleophiles are not as reactive as their C1 counterparts.[159, 160] Vinyl ethers (**45**) were observed as the major products; a result which may partially be a circumstance of having a much larger excess of base in the system.[17]

A successfull synthesis of heterogeneous QM precursor **38** did not seem likely based on the solubility problems encountered during the attempted solution phase benzylation of **36**. However, pursuit of a heterogeneous QM model appeared to be worthwhile based on the predominance of dimer formation in the soluble model/ syringol system. The following sections will describe how the insoluble QM model was modified and eventually prepared.

Modified Synthetic Approach

Polymer-supported QM model **49** was prepared (Scheme 6) according to the general approach taken in the previous heterogenous benzyl ether synthesis. The

Scheme 6

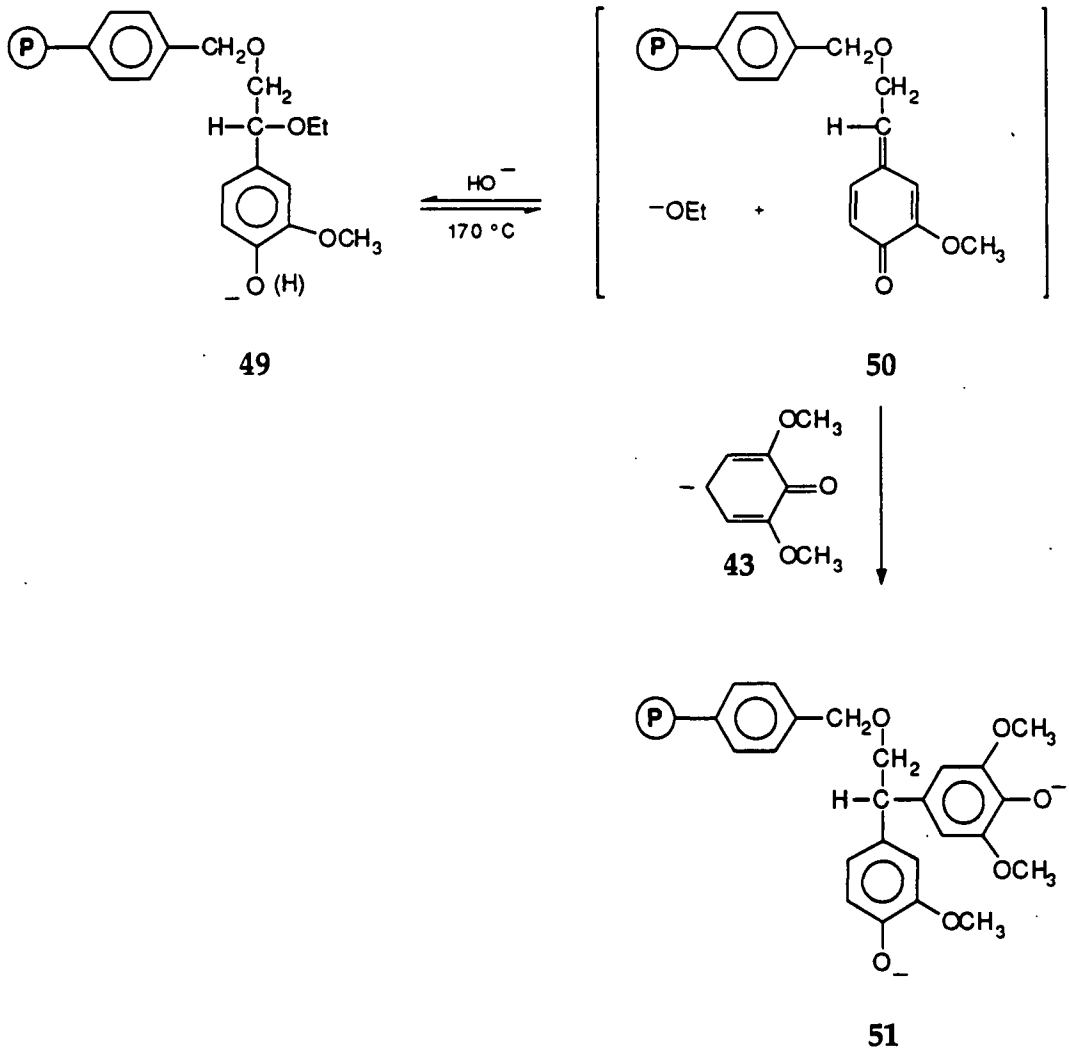


46 47 49 48

first requirement involved the multistep preparation of a protected lignin model, 2-ethoxy-2-(3'-methoxy-4'-allyloxyphenyl)ethan-1-ol (**47**). Both the phenolic and benzylic hydroxyl groups on **47** were protected as ethers leaving the primary hydroxyl group on the β-carbon as the only site available for attachment to the heterogeneous support. Next, the primary alkoxide of **47** was condensed onto iodomethylated polystyrene resin **3** resulting in heterogeneous intermediate **48**. The polymer-supported phenol (**49**) was finally produced by removal of the allyl protecting group. As

shown in Scheme 7, the α-ethoxide on **49** will be lost during the formation of QM 50 and therefore does not have to be removed to activate the supported model.

Scheme 7



49 **50** **51**

The benzyl ether model-to-polymer linkage has demonstrated good stability under alkaline pulping conditions (Fig. 9). Aliphatic β-ether bonds, such as that in

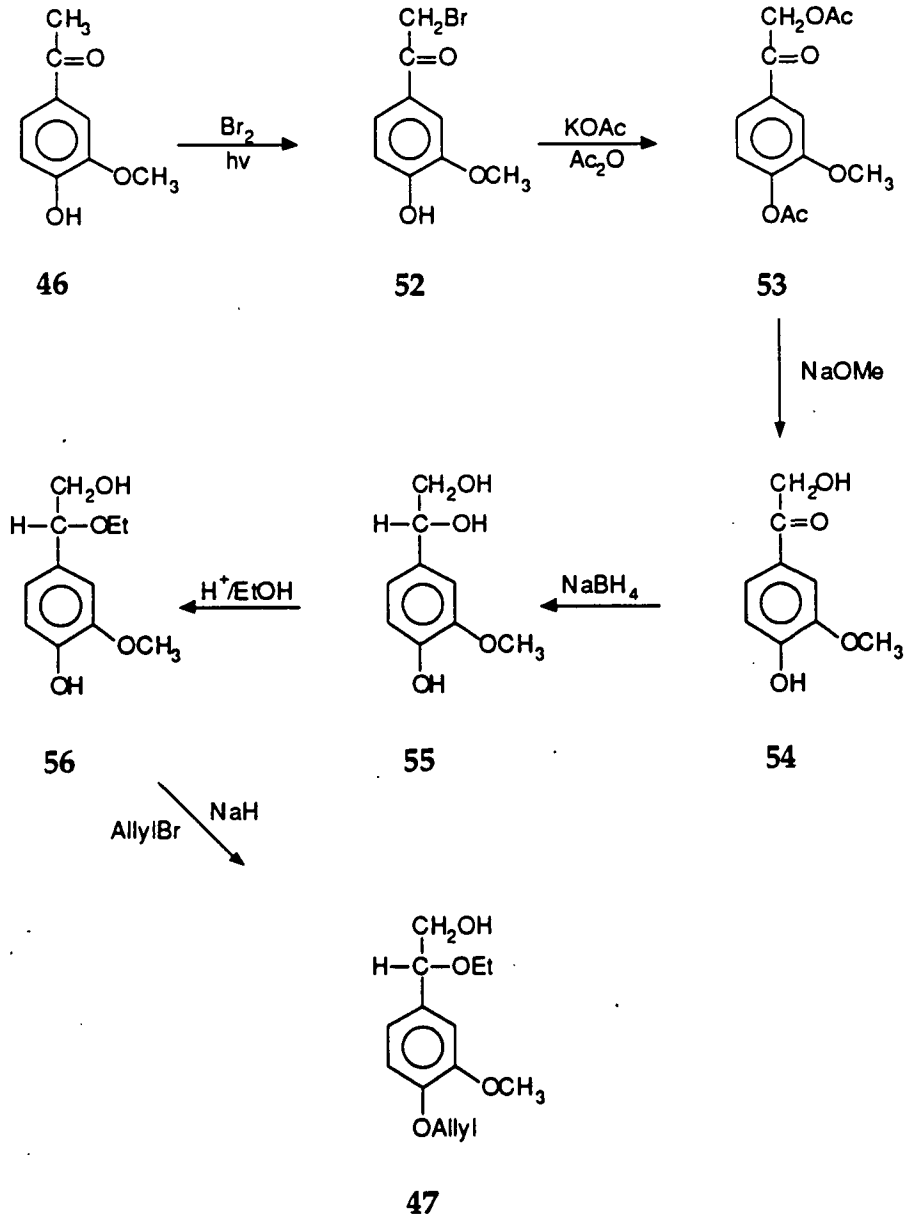
model **49**, are not susceptible to the usual neighboring group-type cleavage experienced by β-aryl ethers during pulping.[161]

Preparation of 2-Ethoxy-2-(3'-methoxy-4'-allyloxyphenyl)ethan-1-ol (47)

The allyl protected α-ethoxy model **47** was prepared from acetovanillone (**46**) as illustrated in Scheme 8. Several modifications to prototype **41** were implemented before arriving at model **47**. First, the six carbon spacer side chain was eliminated since it was suspected of being the major reason as to why benzylation of **41** was not realized. Heterogeneous model **49**, which in essence does not have a "spacer" unit, superficially resembles lignin more closely than does the originally proposed compound (**38**). The lack of a spacer minimizes the possibility of cleavage from the resin through a cyclic (three-membered ring) elimination. The lack of a spacer may also sterically limit the reactivity of the resulting QM (**50**). Second, the α-carbonyl group (on **54**) was reduced (**55**) and finally protected as an ethyl ether (**56**) rather than being reduced to an alcohol while immobilized on the resin. Failure to adequately protect the phenolic site on ketone **54** necessitated the longer synthetic route.

The initial step in the synthetic scheme involved bromination of the aceto methyl group on acetovanillone (**46**) according to the modified method of Hosoya and coworkers[162] as reported by Dimmel and Shepard.[163] A similar synthesis of bromoketone **52** was also reported;[164] however, the extent of bromination using this procedure was less. Bromoketone **52** was isolated as a purple solid which contained residual solvent (dioxane). White crystals of bromoketone could be obtained

Scheme 8

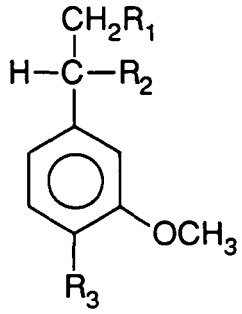


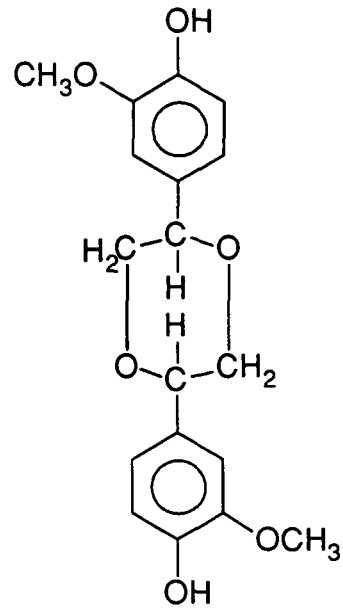
46 52 53 54 55 56 47

upon crystallization of the crude material. Crystallization, however, resulted in approximately a 50% yield loss, and was not required since the crude bromoketone led to pure product, in a moderate yield, in the next step.

Diacetate **53** was prepared from crude bromoketone **52** according to the method of Ferrari and Casagrande.[165] They reported that HCl in methanol readily deacetylated the diacetate giving the corresponding dihydroxy compound (**54**). Although the acidic deprotection routine had been successfully employed by others,[166, 167] incomplete conversions to the dihydroxide were observed when using Ferrari's method. It was found instead that sodium methoxide in methanol could be used effectively in deacetylating **53**. Compared to the reported acidic method, the alkaline system was efficient, easy, and rapid to use in generating the dihydroxide (**54**).

Reduction of the α-carbonyl group of **54** with sodium borohydride gave the glycol (**55**). The boric oxides generated during the reaction made isolation of the glycol difficult; however, a column chromatography procedure proved effective. The glycol was readily characterized as a peracetate (**57**) and silyl derivative (**58**). Holshouser and Kolb[164] reported that treatment of the diacetate (**53**) with lithium aluminum hydride directly produced the glycol (**55**) in moderate to low yield (46%). Several attempts at preparing the glycol with this procedure were unsuccessful.





57, $R_1=R_2=R_3=OAc$
58, $R_1=R_2=R_3=OSiMe_3$
59, $R_1=R_2=OEt$, $R_3=OH$
61, $R_1=R_3=OAc$, $R_2=OEt$

60

The glycol (**55**) was treated with anhydrous hydrogen chloride in ethanol to etherify the benzylic hydroxyl group (**56**). This procedure was based on the selectivity of methanolic hydrogen chloride for benzylic hydroxyl groups as observed by Gierer in the preparation of analogous lignin model compounds.[168-170] Two minor products were observed in the crude product mixture of **56**. They were identified by mass spectrometry as the α,β-diethoxy derivative (**59**) and dimer **60**. Pure α-ethoxide (**56**) could be obtained through recrystallization of the crude product mixture. The α-ethoxide was acetylated (**61**) and examined by ^{1}H-NMR to confirm that the benzylic site had been selectively protected.

Finally, the phenolic site of **56** was protected as an allyl ether to give **47**. The overall yield of allyl-protected model **47** was 18% based on bromoketone **52**.

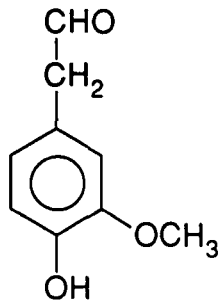
Preparation of the Polymer-supported QM Model

As depicted in Scheme 6, the primary alkoxide of allyl-protected model **47** was initially condensed onto iodomethylated polystyrene resin **3** over a period of several days giving heterogeneous intermediate **48**. The alkoxide was generated in situ by treatment of **47** with NaH in THF. A significant level of coupling was suggested by the elemental analysis of product resin **48**; the iodine content had dropped from 31.1 to 9.32%. Presence of the supported model was confirmed by the FTIR spectrum which showed moderate olefinic (allyl) C-H absorptions at 996 and 929 cm^{-1} in addition to several strong C-O stretch signals ranging from 1263 to 1103 cm^{-1}.

The residual benzyl iodide units on heterogeneous intermediate **48** were converted to nonreactive methyl ethers by treatment with sodium methoxide in methanol. The iodine content fell from 9.32 to 1.94%; no changes were readily apparent in the FTIR spectrum.

The final step in the preparation of polymer-supported model **49** involved removal of the allyl group thereby generating the free phenol. Displacement of the allyl group by isomerization with tris(triphenylphosphine)rhodium(1) chloride (TTPPR) and 1,4-diazabicyclo[2.2.2]octane (Dabco) to a prop-1-enol ether followed by acid hydrolysis had previously been effected in good yield. Such was not the case

with the current model which demonstrated a sensitivity to acidic conditions. Allyl-protected compound **47** was used as a test substrate to determine the general stability of the model to the conditions encountered during removal of the allyl group. Treatment of **47** with TTPPR/Dabco in a refluxing mixture of ethanol/benzene/water gave the corresponding prop-1-enol ether as desired. However, subsequent reaction of the intermediate ether with dilute HCl in acetone resulted in a product mixture containing the desired phenol **56** (35%) in addition to a species tentatively identified by its mass spectrum as aldehyde **62** (48%).



62

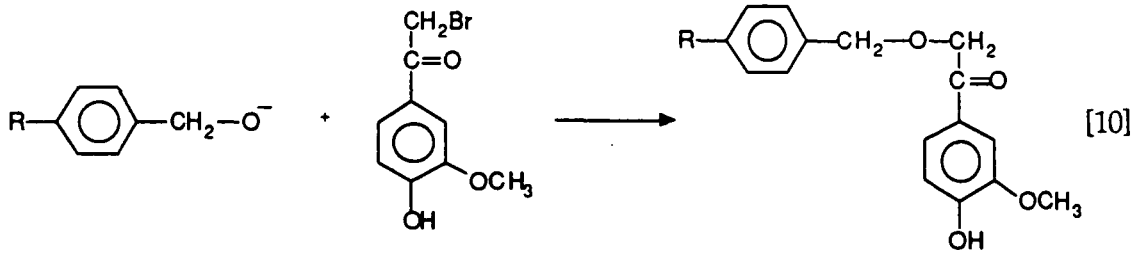
Gigg and Warren[171] reported that mercuric chloride in the presence of mercuric oxide (yellow form), in an acetone/water solvent mixture, readily cleaved prop-1-enol ethers in the presence of acid labile groups; benzyl ether bonds were shown to be stable under the prescribed reaction conditions. Hence, treatment of model **47** with TTPPR/Dabco followed by $HgCl_2$/HgO yielded the desired phenol **56** with no traces of aldehyde **62**.

Mercuric oxide, which is present to scavenge the HCl generated during the cleavage reaction, is not readily soluble in the acetone/water solvent system. Insoluble reagents are, in general, not effective in polymer-supported systems.[138] Other acid scavengers, such as pyridine, are known to inactivate mercuric chloride.[172, 173] Treatment of a sample of the prop-1-enol with mercuric chloride alone gave primarily the phenol (**56**) with low levels (less than 10%) of the aldehyde (**62**). The minor side reaction observed in the soluble system may not be as prevalent in the heterogeneous case since (a) the generation of an aldehyde would require cleavage from the support and (b) the supported model may not be as accessible to the low levels of HCl as in the solution phase system.

Etherified heterogeneous intermediate **48**, based on the preliminary work with soluble model **47**, was treated with TTPPR/Dabco followed by $HgCl_2$. The extent of allyl group removal was qualitatively determined by FTIR. After two treatments, the allyl signals were effectively minimized; a strong hydroxyl signal was concomitantly observed confirming that the free phenol had been generated. Carbon-13 NMR was also used to show that the allyl groups had been removed. Analysis of the reaction liquor after treatment of the resin with $HgCl_2$ revealed no traces of the lignin model.

Another presumably more straight forward synthesis of **49** could involve the coupling reaction outlined in Eq. 10, followed by reduction of the supported product with sodium borohydride.[138] The attractive aspects of this route are that (a) no

protecting group is needed at the phenolic site of bromoketone **52**, which makes the overall preparation shorter, and (b) synthesis of the polymer-supported benzyl alcohol[174] and subsequent reduction methods are documented. Attempts at generating heterogeneous ketone **65** were aborted, however, after several attempts at preparing the soluble counterpart (**66**) were unsuccessful.



[10]

63, R=P
64, R=H

52

65, R=P
66, R=H

Model Loading Determination

As before, two approaches were taken in determining the quantity of model on the polymer support. A loading of 1.33 mmol/g was determined from the weight gain of the resin during the initial coupling step of the heterogeneous synthesis. As noted earlier, the gravimetric method provides only an estimate of the quantity of model on the polymer.

The second approach involved cleaving the benzyl ether model-to-polymer linkage with iodotrimethylsilane (ITS) and quantifying the amount of cleaved material by GLC. This method also provides further structural proof that the

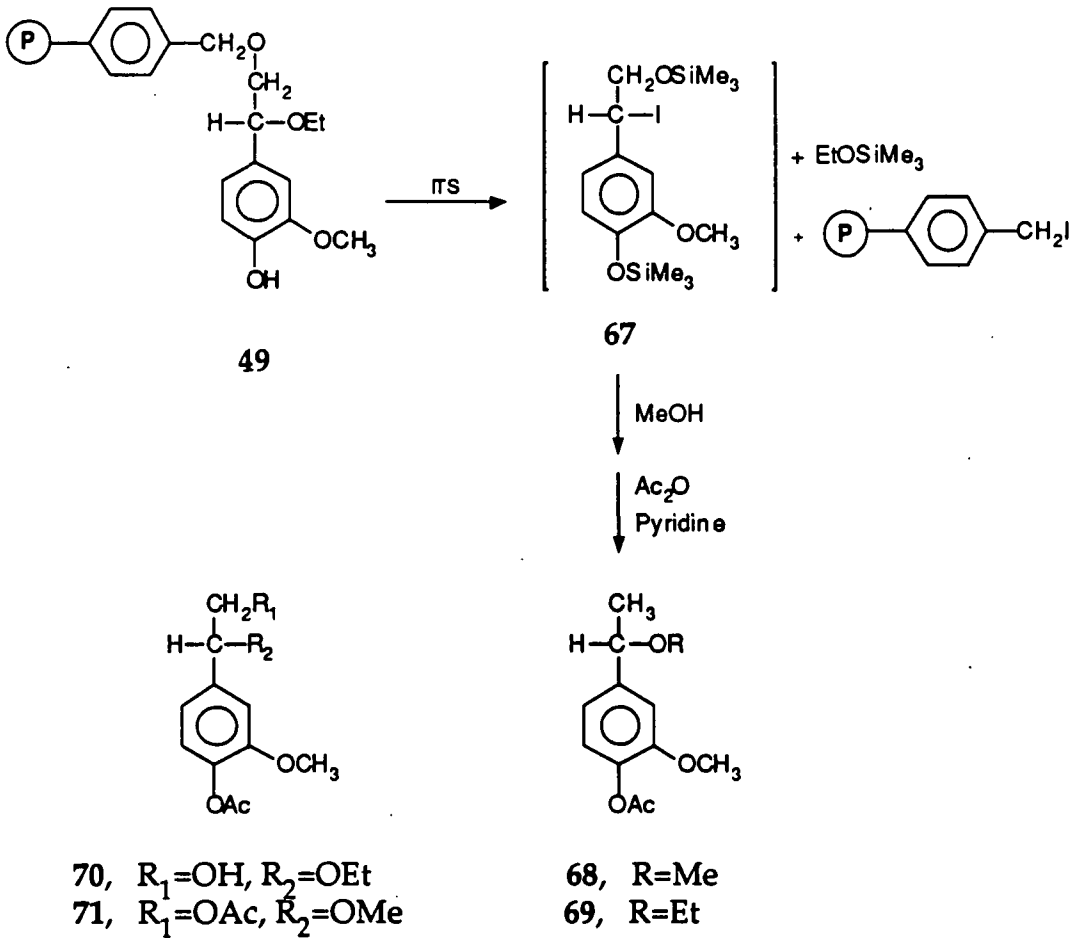
intended model had been successfully prepared. The loading value obtained by the ITS technique was 0.83 ± 0.03 mmol/g. Analysis of the ITS treated resin by FTIR showed that not all of the model could be removed since some residual C-O signals were observed. A strong benzyl iodide signal was observed, however, indicating that a majority of the model had been cleaved from the support.

Compound **68** (Scheme 9) was identified as the soluble cleavage product after treatment of the heterogeneous model (**49**) with ITS. As illustrated in Scheme 9, the ITS reacts with both benzyl ether bonds resulting in free intermediate **67**. When the reaction is quenched with anhydrous methanol, the α-iodo group is displaced along with the β-silyl group (through an unconfirmed mechanism) resulting in the corresponding β-methyl/α-methoxy system (**68**). Quenching of the reaction with ethanol results in the analogous α-ethoxy compound (**69**). Treatment of soluble α-ethoxy model **56** (Scheme 8) with ITS also gives **68**, thus confirming that the desired model was successfully coupled to the polymer support. Compounds **70** and **71** were observed (11 and 6% relative to **68**) as minor products in the ITS reaction.

Summary of the Heterogeneous Support Evaluation and Preparation of the Insoluble Ligninlike Models

Two macroreticular polystyrene resins, Amberlite XE-305 and Biobead SM-16, were examined as potential supports for lignin model compounds. The more highly crosslinked (16%) resin, Biobead SM-16, showed limited synthetic reactivity and was therefore not suitable as a supporting matrix. The Amberlite XE-305, a

Scheme 9



more lightly crosslinked (3-4%) resin which had been used successfully by other researchers,[74, 75] gave correspondingly high synthetic yields. Based on its high synthetic potential and large (1400 Å) average pore diameter, the Amberlite XE-305 resin was again employed as the supporting matrix. The Amberlite network was shown, theoretically and by determination of an activation energy, not to impose mass transfer limitations under simulated soda pulping conditions.

A highly functionalized (0.81 ± 0.04) polymer-bound lignin model (**6**) was prepared using a benzyl ether model-to-polymer linkage. The ligninlike monomer, guaiacylpropanol, which was attached to the support through its primary alcohol, could be selectively protected at the phenolic site by several reagents. The allyl group proved to be the best protecting group tested in terms of stability during benzylation and high yield selective deprotection in the presence of benzyl ethers. The polymer-supported benzyl ether bond, unlike the prototypic trityl ether linkage, was found to be inherently stable after an initial loss of model under alkaline pulping conditions. Some resin morphology changes were observed upon thermal treatment of the bound model.

A supported model (**49**) potentially capable of generating a (heterogeneous) QM under alkaline pulping conditions was prepared and characterized. A loading value of 0.83 ± 0.03 mmol/g was determined by the ITS method. The initial model design, which incorporated a six carbon side chain (**38**, Scheme 5) was abandoned due to foreseeable difficulties in preparing the heterogeneous substrate. The final synthesis of supported model **49** required nine steps overall but, in general, followed documented synthetic techniques.

Benzyl ether cleavage <u>via</u> iodotrimethylsilane was demonstrated to be a simple and reproducible method for determining the amount of accessible model. This method was not, however, quantitative for the highly loaded resins. Analyses by SEM-EDS showed that the model distributions throughout the resin were

homogeneous and that the interior macroporous regions of the polymer network were accessible to ITS. Spectral characterization of the resin intermediates and products by FTIR and high resolution ^{13}C-NMR confirmed the chemical analyses of the heterogeneous models.

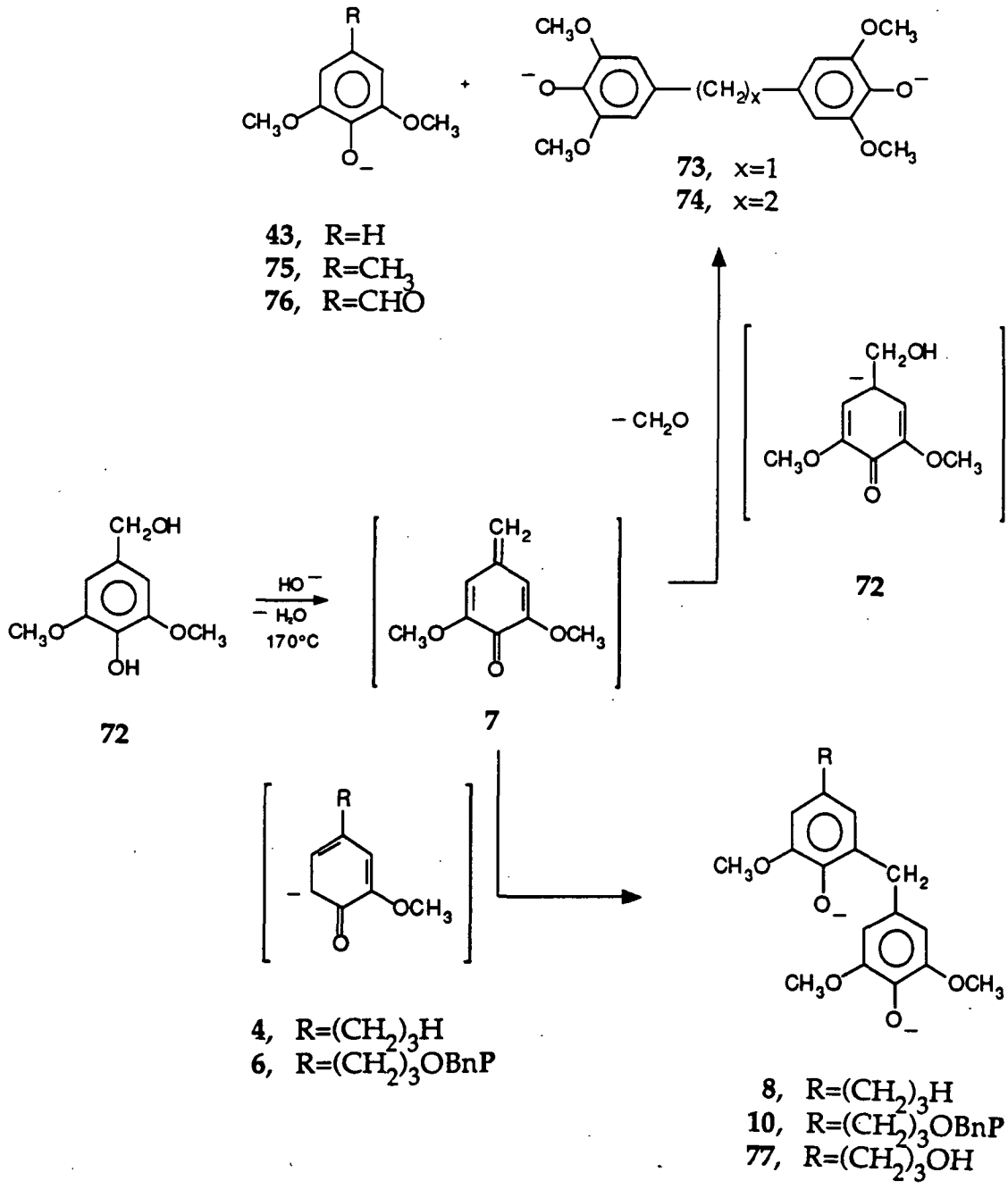
CONDENSATION REACTIONS

Polymer-supported Phenol System

The first heterogeneous reaction system to be investigated is depicted in Scheme 10. The initial, and most likely the slow,[17] step of the reaction sequence is the formation of a QM (**7**) from syringyl alcohol (**72**). Once generated, the QM can react with its precursor phenol (self-condensation) or with the added soluble (**4**) or insoluble (**6**) guaiacylpropane carbanions.

The self-condensation of syringyl alcohol (**72**) under soda pulping conditions has been previously reported.[18] The major product, disyringylmethane (**73**), results from attack of a C1$^-$ anion of syringyl alcohol (**72**$^-$) on the α-carbon of a syringyl QM (**7**), followed by loss of formaldehyde. Trace amounts of a second dimer, bisyringyl (**74**), were also detected. Bisyringyl is presumably generated when two α-carbon radicals combine. Minor quantities of several noncondensation products, monomers **43**, **75**, and **76**, were also identified. In the syringyl system, methoxyl groups at both the 3 and 5 aromatic ring positions prevent the formation of trimers and other

Scheme 10


R
CH3O
OCH3
O−
+
CH3O
OCH3
−O
(CH2)x
O−
CH3O
OCH3
73, x=1
74, x=2
43, R=H
75, R=CH3
76, R=CHO
− CH2O
CH2OH
CH3O
OCH3
O
72
CH2OH
CH3O
OCH3
OH
HO−
− H2O
170°C
CH2
CH3O
OCH3
O
72
7
R
− OCH3
O
4, R=(CH2)3H
6, R=(CH2)3OBnP
R
CH3O
CH2
O−
CH3O
OCH3
O−
8, R=(CH2)3H
10, R=(CH2)3OBnP
77, R=(CH2)3OH

higher order condensation products which are observed with the C3 monomethoxy compound vanillyl alcohol.[19, 175]

For this study, the reactions of syringyl alcohol (**72**) with guaiacylpropane (**4**) and polymer-bound guaiacylpropanol (**6**) were of primary interest. To directly compare the homogeneous (soluble system) and heterogeneous (supported system) reaction rates, the ratio of reactants in the two systems must be the same. However, the exact amount of supported guaiacylpropanol (**6**) accessible to the pulping liquor was not known. The quantity of **6** employed was based on the ITS loading value which represents a minimum level of supported model. In both systems, a 25% excess of guaiacylpropane (**4** or **6**), vs. syringyl alcohol, was used. The solution phase reaction was conducted in the presence of inert polymer-bound benzyl ethoxide in order to make the reaction environment and liquor work-up more analogous to that of the heterogeneous system.

In both the soluble and two-phase reactions, a new interunit condensation product, the C5-Cα dimer (**8** or **10**), was observed in addition to the standard syringyl-syringyl products (Scheme 10). The mechanism for the formation of C5-Cα dimer is similar to that of disyringylmethane (**73**), except that the nucleophile is the $C5^-$ anion of guaiacylpropane ($\mathbf{4}^-$ or $\mathbf{6}^-$). The level of C5-Cα dimer (**8**) formed in the soluble system was compared to the amount of dimer (**10**) produced in the analogous two-phase environment (Fig. 10).

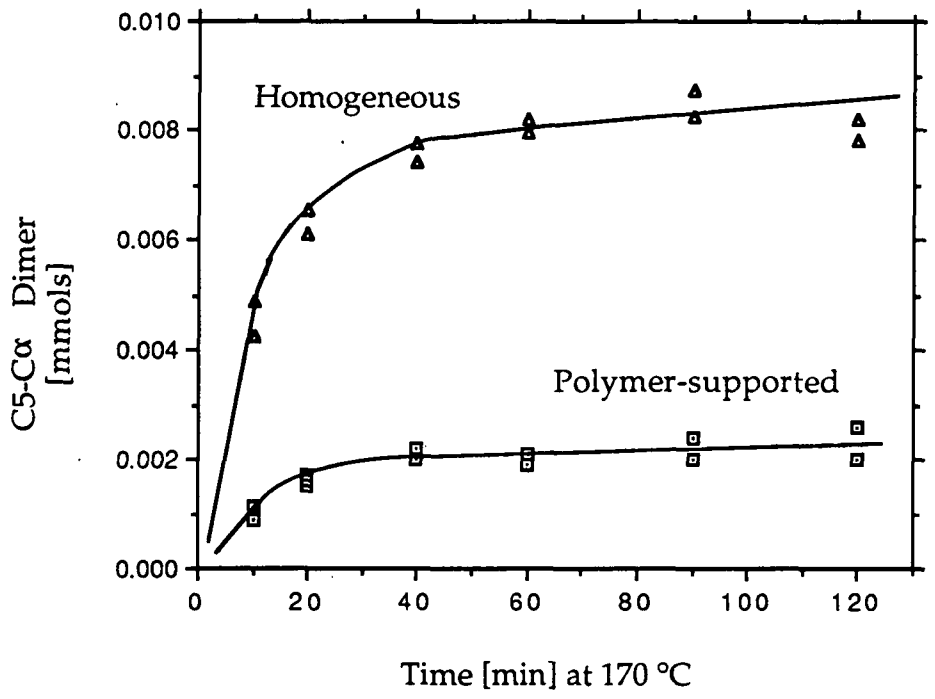


Figure 10. Concentration of the C5-Cα dimer vs. time at temperature.

The formation of soluble C5-Cα dimer (**8**), as shown in Fig. 10, was rapid and extensive. The final yield of dimer **8**, the major product, was 40% based on the initial level of syringyl alcohol. As expected, heterogeneous C5-Cα dimer (**10**) formation was slower and lower in yield (11%). A significant level of **10** was, however, observed early (10 min) in the cook. Only trace quantities (< 0.01 mmol/g) of a soluble C5-Cα dimer (**77**) were found in the heterogeneous reaction solution indicating that the resin preconditioning was successful.

In the homogeneous system, the final concentration of phenol-syringyl C5-Cα dimer **8** was greater, by a factor of 2.5, than the syringyl-syringyl C1-Cα dimer **73**. However, no conclusive evidence on the relative reactivities of the C5 and C1

nucleophiles could be ascertained from these data, since the Cl^- anion and QM concentrations were not known. As previously noted, rate studies incorporating similar systems have shown that the C1 position is more reactive than the C5.[159, 160]

The soluble reaction by-products, disyringylmethane (**73**), syringol (**43**), 4-methylsyringol (**75**), and syringaldehyde (**76**), did not follow any consistent patterns between the two systems. The latter three products were present at significantly higher levels at 170 °C than at 150 °C. Bisyringyl (**74**) was not observed in either product mixture.

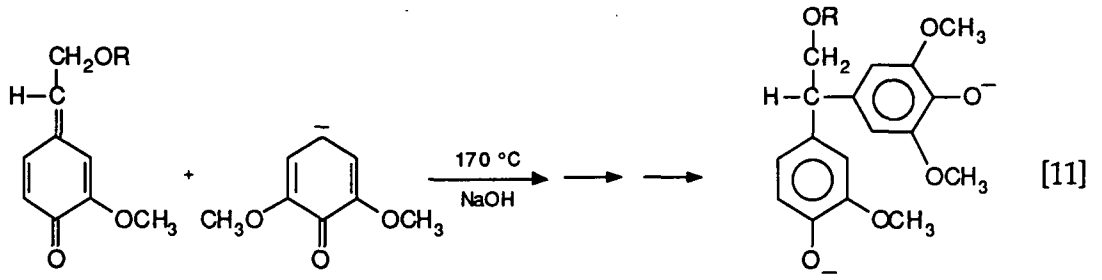
Quantitative kinetic expressions were not determined because (a) the amount of accessible polymer-bound guaiacylpropanol was not accurately known, (b) the local concentration between the soluble and insoluble systems may be quite different, (c) the formation of the minor products was inconsistent, and (d) an analytical GLC response factor, based on the value for the homogeneous dimer, was assumed for the heterogeneous C5-Cα dimer due to the unavailability of **77**.

Heterogeneous reaction rates have, in general, been found to be slower than in the analogous homogeneous reactions.[71, 72] The slower rates, in systems without mass transfer limitations, have been ascribed to be the result of a greater loss in internal degrees of freedom when forming the heterogeneous transition state.[71] Polyelectric and steric factors may also contribute to the observed heterogeneous rate decrease. Rates in supported systems could be, however, more dependent upon the

local concentration of immobilized reactant than on the actual rate of the specific chemical transformation.[93b]

Polymer-supported Quinone Methide System

The second set dual homo- and heterogeneous reactions to be studied is outlined in Eq. 11 (refer also to Scheme 7). As illustrated, the primary condensation product, a C1-Cα dimer (**79** or **51**), results from addition of the soluble C1 nucleophile of syringol (**43**) to a simple QM (**78** or **50**). The yield of soluble C1-Cα dimer **79** was compared to that of insoluble dimer **51**.



[11]

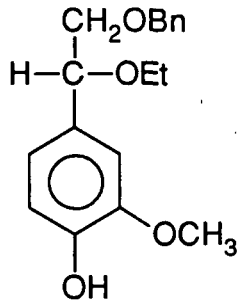
78, R=Bn
50, R=BnP

43

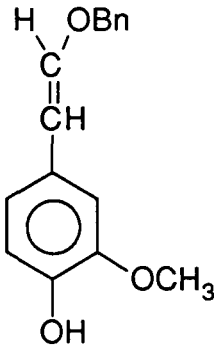
79, R=Bn
51, R=BnP

Benzylation of α-ethoxy precursor **47** followed by removal of the allyl protecting group yielded compound **80**, the soluble counterpart of heterogeneous QM model **49**. Soluble model **80** was cooked at 170 °C with three equivalents of syringol (**43**) in a weak (0.050M) alkaline solution (Eq. 11). The conditions employed were those that yielded a high percentage of a C1-Cα dimer (**44**) with soluble model prototype **42** (Eq. 9). Reaction times were initially limited to 15 and 40 min at 170 °C.

After the standard methylation work-up, the samples were analyzed by GLC and GC/MS. A high yield (64%) of C1-Cα dimer (**79**) was detected in the 15 min sample; over 85% of the starting material (**80**) had been consumed. A low yield of a vinyl ether (**81**) was detected along with lesser amounts of several unidentified products. Extending the cook to 40 min decreased the relative level of vinyl ether present but otherwise had no major effect.



80



81

A test of heterogeneous QM model **49** for C1-Cα dimer formation was conducted under the same conditions as the solution-phase trial (Eq. 11/Scheme 7). A sampling time of 40 min was employed to allow for the slower rate of the heterogeneous reaction. Analysis of the cooking liquor revealed that the level of syringol, relative to an internal standard, was much higher than in the soluble model case which suggested that the extent of condensation, as anticipated, was less. No detectable levels of cleaved model were observed in the reaction liquor. This was

surprising since some initial instability was observed with the supported guaiacylpropanol model (**6**).

The reacted resin, after it had been washed and dried, was treated with ITS. No heterogeneous C1-Cα dimer (**51**) was detected. The level of starting material had decreased from an initial loading of 0.83 to 0.43 mmol/g; it should be noted that the ITS method cannot distinguish between those units of starting material which have or have not undergone an alkali induced α-ethoxide/hydroxide exchange. Only one new species, which appeared to result from a Claisen rearrangement of a residual allyl unit, as previously detailed for the bound guaiacylpropanol model, was observed in minor quantities. No other signals directly attributable to a reaction product were discernible.

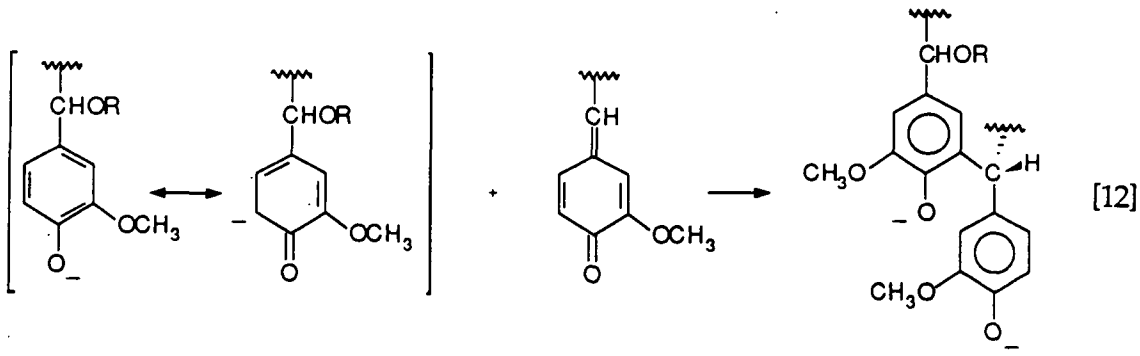
Likewise, the FTIR spectrum of the reacted resin was nearly the same as that of an unreacted sample with the exception of stronger hydroxyl (3600-3100 cm^{-1}) and weaker aliphatic ether (1100 cm^{-1}) absorbances. The noted changes in signal intensity arise from the conversion of α-ethoxy to hydroxyl groups which indicates that heterogeneous quinone methides were formed during the cook. Generation of a weak unassigned olefinic signal at 1649 cm^{-1} was also observed. Weak α- and β-carbon signals in the ^{13}C-NMR spectrum of the unreacted starting material (**49**) precluded use of this technique for analyzing the reacted resin.

Several hypotheses to explain the inactivity of the heterogeneous system seemed plausible. One speculation was that steric factors prevented proper access to

the heterogeneous QM; the other limiting factors of insoluble systems, entropy and polyelectrolyte effects, would also contribute to hindering dimer formation. Steric factors were a concern with the modified model (**49**) when the six carbon spacer side chain was eliminated.

Also, the heterogeneous model could possibly undergo intraresin condensation since the bound appendage can, through resonance, form a C5 anion (Eq. 12). Intraresin condensation would effectively increase the degree of crosslinking therefore limiting the accessibility of the ITS reagent. This would account in part for the incomplete recovery of reaction products or starting material. The limited ITS accessibility and requirement that two benzyl ether bonds be cleaved in a product such as **82** could explain why no self-condensation dimer was observed.

A third possibility was that a vinyl ether-type compound (e.g. **81**) was formed as the major insoluble appendage. Vinyl ethers, generated by abstraction of a Cβ proton,[17] have been observed as major products in other soda cooked model systems.[44, 176] A substantial degree of benzyl ether bond cleavage was observed when 4-benzyloxyphenol was exposed to ITS for 25 min at room temperature; a result which shows that benzyl ether-unsaturated carbon bonds are labile in ITS. Therefore, vinyl ethers should have been observed in the reaction product mixture had they been formed on the resin to a significant extent.



[12]

[∿∿ = to polymer]

82

In an attempt to validate the latter two hypotheses, a control cook of soluble model **80** was performed in 0.050M NaOH for 15 and 40 min at 170 °C. As before, the reaction products were methylated with dimethylsulfate prior to qualitative analysis by GC/MS. Under this set of conditions, no C5-Cα dimer was identified in the product mixture. Absence of any C5-Cα dimer would suggest a low probability of intramolecular self-condensation on the resin. The intraresin condensation theory (Eq. 12) cannot, however, be totally disregarded since the local quantity of supported model is higher than in the soluble system. The close proximity of immobilized appendages may foster intraresin reactivity.

The control test also did not support the vinyl ether proposal. A moderate amount of vinyl ether **81** was observed at the early time period; by the end of the cook the level had significantly decreased. The major product, at approximately 32%, was the starting material which had undergone an α-ethoxide/hydroxide

exchange. In addition to the vinyl ether, several other minor components, whose structures could not be positively confirmed, were detected.

A likely scenario, in light of the results from the solution phase control test, may be that the modified polystyrene network effectively creates an environment in which the bound QM is shielded from the syringol nucleophile thus inhibiting heterogeneous dimer formation. The two-phase system therefore behaves as in the homogeneous control where the starting material is slowly consumed yielding an assortment of minor compounds which cannot readily be removed from the resin.

Efforts to promote heterogeneous condensation were made by modifying the reaction conditions. All endeavors were unsuccessful and led to lower recoveries, after treatment with ITS, of starting material. The conditions employed were (a) increasing the reaction time under current conditions (0.05M NaOH, three eq. of syringol) to two hours, (b) raising the base concentration, while maintaining three eq. of syringol, to 1.00M, and (c) using ten eq. of syringol which required an increase in alkali concentration to 0.10M.

In spite of low returns of starting material, no other signals associated with reaction products were prevalent. Resin morphology changes could account for the nonquantitative recovery of starting material or products as was the case in the supported guaiacylpropanol system. It is doubtful, however, that such changes would exclude the presence of heterogeneous products to the degree observed.

Several efforts were made to remove some product from the reacted resin. A second extended (15 hr) application of ITS to a once treated resin yielded only a trace of starting material. Another method known to cleave heterogeneous benzyl ether bonds, acetolysis, was also investigated. Acetolysis did not work efficiently with the bound guaiacylpropanol model (**6**) but did with a supported carbohydrate.[75] Tests on soluble model **80** were successful; the benzyl ether bond was quantitatively cleaved without excessive model degradation. The subsequent acetolysis of an ITS resin, however, yielded only minor quantities of the starting material.

Reasons for the failure of the ITS and acetolysis methods to remove reacted model from the resin are not clear. The FTIR spectrum of an ITS resin showed a weak benzyl iodide signal at 1155 cm^{-1} which is consistent with the visible lack of released material. A complimentary SEM-EDS analysis indicated that the distribution of iodine across the resin was still homogeneous. The impotency of the ITS and acetolysis methods lends support to the intramolecular self condensation hypothesis in which overall reagent accessibility could be limited due to a higher degree of crosslinking.

Summary of the Heterogeneous Condensation Reactions

Reaction of guaiacylpropane (**4**) or supported guaiacylpropanol (**6**) with the QM of syringyl alcohol (**7**), under soda pulping conditions (1M NaOH, 170 °C, 2 hr), resulted in the formation of C5-Cα dimers **8** and **10**, respectively. The yield of insoluble C5-Cα dimer **10** was 28% of the level of corresponding condensation product

8 observed in the analogous soluble system. The level of C5-Cα dimer **10** formed in the two-phase system exceeded expectations since the soluble co-dimerization species, syringyl alcohol (**72**), had several alternative "soluble" pathways for consumption (Scheme 10). The high local concentration of polymer-bound guaiacylpropanol (**6**) may have greatly increased the probability of condensation for those syringyl QMs (**7**) that entered, or were formed in, the resin matrix. The effect on the degree of heterogeneous condensation of varying the number of side chain carbons on the supported phenol (e.g. from three to two or one) was not investigated. The lower, but significant level of heterogeneous condensation suggests that soluble lignin units are capable of condensing onto, and forming alkali stable bonds with, the insoluble lignin gel during the course of an alkali cook. The inhibition of such two-phase condensation reactions should lead to lower levels of residual lignin.

After several design changes, a simple polymer-supported model (**49**) capable of forming a QM was prepared and characterized. The heterogeneous substrate did not react with a soluble ligninlike component under any variety of conditions, whereas the corresponding soluble model (**80**) rapidly transcribed to the desired C1-Cα condensation dimer. Deductions from a soluble control reaction of model **80** suggest that steric factors are primarily responsible for preventing condensation in the heterogeneous system. A new model that is further removed from the polystyrene backbone would have to be designed and tested in order to conclusively prove this hypothesis. Intraresin condensation, if it occurs, might be eliminated by implementing a syringyl-type aromatic nuclei. Failure to recover any significant

quantity of reaction product from the resin indicates that the model has been modified by the cook into a form that does not readily relent to cleavage by extended treatment of ITS or acetolysis. The absence of heterogeneous dimer suggests that condensation of dissolved lignin moieties onto the lignin gel may not actively begin until later in the cook when a higher degree of lignin accessibility has been attained. This finding is consistent with other research[6, 48] which has indicated that condensation is more prevalent during the later stages of alkali cooks.

CONCLUSIONS

The most salient conclusions of this work can be enumerated as follows:

1. Reaction of supported guaiacylpropanol with the soluble QM of syringyl alcohol in 1.00M NaOH at 170 °C yielded a heterogeneous C5-Cα dimer. The yield of dimer in the analogous soluble system was four times as great under the imposed reaction conditions. This result suggests that soluble lignin units can condense onto the insoluble lignin gel during the course of alkaline pulping.

2. No concentration of a C1-Cα dimer was observed when a heterogeneous QM was reacted, under soda pulping conditions, with a soluble syringyl carbanion. Reaction of the corresponding soluble QM with the syringyl nucleophile yielded a high level of dimer, which indicates that steric constraints may be prohibiting the potential two-phase interactions. These data do not preclude that condensation in the gel phase may occur later in the cook when reaction sites are more accessible.

3. The above results confirm a lower degree of reactivity in heterogeneous systems and suggest that reactions of soluble models may not accurately reflect many pulping reaction rates.

In addition, the following was found:

4. A lightly crosslinked (3-4%) macroreticular resin, Amberlite XE-305, which had been successfully used by fellow researchers[74, 75] as a support for other woodlike

models, again demonstrated a high synthetic aptitude. A more highly crosslinked (16%) macroreticular polystyrene resin, Biobead SM-16, was found to be limited in its usefulness as a polymeric support due to low synthetic activity.

5. The large (1400 Å diameter) macroporous network of Amberlite XE-305 was shown, theoretically and by determination of an activation energy, not to impose mass transfer barriers to infusing reactants under high temperature alkaline conditions. Therefore, the observed heterogeneous reaction rates should reflect the inherent rate of chemical reaction.

6. The trityl ether model-to-polymer linkage was readily severed under the conditions encountered during alkaline pulping and was thus not well suited for the intended studies.

7. The stability of the benzyl ether model-to-polymer linkage[75] under alkaline pulping conditions was confirmed. The overall level of stability was dependent upon the particular model involved.

8. The allyl group can be used effectively for selectively protecting phenols. The rate of deprotection for the resulting aromatic ethers was, however, more sluggish than that reported for aliphatic allyl ethers.

9. High resolution ^{13}C-NMR can be used to structurally characterize the lignin-like models immobilized on the Amberlite XE-305 resin.

10. Iodotrimethylsilane is an effective reagent for selectively cleaving the heterogeneous benzyl ether linkage. Measuring the amount of released model by GLC provides a simple and reproducible way of determining the level of model loading. Residual quantities of model were, however, detected on the resin after treatment by ITS. An x-ray analysis of the ITS treated resin revealed that the reagent was able to penetrate the innermost regions of the macroporous network. Therefore, the model remaining on the resin must reside in highly inaccessible segments of the bead which, most likely, would not be readily contacted by alkaline pulping liquors.

EXPERIMENTAL METHODS

GENERAL

Proton and ^{13}C-NMR spectra were recorded on a Jeol FX100 spectrometer at 100 and 25 MHz, respectively, using TMS as an internal reference. High resolution ^{13}C-NMR spectra (90 MHz) of the polymer-supported compounds in $CDCl_3$ were obtained by Spectral Data Services[177] on a 360 MHz instrument according to the method of Ford and coworkers.[132] Infrared spectra were recorded on a Perkin-Elmer Model 700 infrared spectrometer and standardized with polystyrene. Infrared spectra of the heterogeneous models were obtained as KBr pellets with a Nicolet 7199 Fourier transform spectrometer. The x-ray data were recorded with a Tracor Northern TN-2000 energy dispersive spectrometer interfaced with a Jeol 35C scanning electron microscope.

Gas-liquid chromatography (GLC) was performed on a Hewlett-Packard 5890 instrument interfaced with a Hewlett-Packard 3392 integrator. Gas chromatographic analyses were performed on a glass column (6 ft. x 2 mm ID) packed with OV-17 (3%) on Supelcoport (80-100 mesh). The general operating conditions were as follows: inj. temp. 285 °C, det. temp. (FID) 300 °C, helium carrier gas at 20 mL/min, program 100 °C (1 min) to 285 or 300 °C (5-10 min) at 10-15 degrees/min. Analytical GLC response factors were calculated according to standard methods.[75] A Hewlett-Packard 5985 instrument was used for GLC mass spectroscopy (GC/MS). The GC/MS

interface was maintained at 250 °C. Electron impact (EI) MS used helium as the carrier gas, a source temp. of 200 °C, and an ionization voltage of 70 eV.

Melting points were recorded on a Thomas-Hoover capillary apparatus and are uncorrected. Elemental analyses were performed by MicroTech Laboratories, Indianapolis, IN. The methoxyl analyses of the heterogeneous models were performed by Chem-Lig International, Schofield, WI.

Amberlite XE-305 was purchased from Polysciences, Inc. Warrington, PA. The Biobead SM-16 resin was obtained from Bio-Rad Laboratories, Richmond, CA. All solvents employed, unless indicated otherwise, were A.C.S. reagent grade. Reagents and starting materials were obtained from Aldrich Chemical Co., Milwaukee, WI.

Preparations involving the use of sodium hydride (97%) incorporated anhydrous solvents and were conducted under a dry nitrogen atmosphere in oven-dried glassware until the reaction was quenched. An overhead stirring apparatus was employed in all resin modification reactions to minimize mechanical damage to the polymer support. All column chromatography purifications employed silica gel 60 (70-230 mesh ASTM) as the stationary phase.

SOLVENTS AND REAGENTS

Acetic Anhydride

Reagent grade acetic anhydride was fractionally distilled and stored under a nitrogen atmosphere away from light.[178]

Acetonitrile

Reagent grade acetonitrile was dried over 4Å molecular sieves and stored under a nitrogen atmosphere.

Allyl Bromide

Distilled allyl bromide was obtained from M. Bovee.[75]

Anhydrous Methyl Alcohol

A mixture of magnesium turnings (10 g), iodine (0.5 g), and methanol (50 mL) was gently heated until the magnesium had been completely oxidized.[178] An additional volume of methanol (1.5 L) was added, refluxed for 2 hr, and fractionally distilled. The anhydrous solution was stored under a nitrogen atmosphere.

Anhydrous Propyl Alcohol

Reagent grade propanol (350 mL) was refluxed (2.5 hr) and fractionally distilled over 11 g of calcium oxide. The middle fraction of distillate was dried over 45 g

of potassium carbonate, filtered, and further dried over 20 g of calcium hydride. The propanol was again filtered and distilled. The anhydrous material was stored under nitrogen in a dark bottle.[178]

Benzene

Reagent grade benzene (500 mL) was shaken with 50 mL of concd. sulfuric acid, then washed successively with 100 mL of water, 50 mL of 6M NaOH, and water (100 mL). The benzene was finally dried and fractionally distilled over phosphorus pentoxide.[178] The dry benzene was stored under a nitrogen atmosphere.

Benzyl Bromide

Benzyl bromide was prepared according to the method presented by Perrin et al.[178] This consisted of washing the benzyl bromide (70 mL) with concd. sulfuric acid (2x50 mL), then water (50 mL), 10% aq. sodium bicarbonate (2x30mL), and water (3x50 mL), followed by drying over magnesium sulfate. The material was then fractionally distilled in the dark under reduced pressure. The purified material was stored in a dark bottle under nitrogen.

N,N-Dimethylformamide (DMF)

For general synthetic purposes, the DMF was dried over 4Å molecular sieves and stored under nitrogen. The DMF was distilled[75] before use in the unsuccessful coupling of allyl-protected guaiacylpropanol (**25**) to iodomethylated resin **3**.

Oxygen-free Distilled Water

Approximately 2 L of distilled water was boiled down to 1200 mL. The intended container was rinsed first with 400 mL of the boiling water before the remaining 800 mL was added. Nitrogen was then bubbled through the water for 3 hr while it cooled. The treated water was stored under nitrogen for no longer than two days before use.[179]

Pyridine

Reagent grade pyridine (1 L) was refluxed over potassium hydroxide (400 g) for 4 hr and fractionally distilled.[178] The anhydrous solvent was stored under nitrogen in a dark bottle.

Sodium Methoxide and Sodium Ethoxide

Under anhydrous conditions, freshly cut sodium metal was added to a stirring solution of anhydrous methanol or absolute ethanol. The sodium metal was rinsed in hexane followed by a solution of the intended alcohol before being added to the main reaction vessel. The sodium metal was added slowly to avoid generating excessive heat. The resulting solutions were stored under a nitrogen atmosphere.[75] For quantification purposes, the sodium methoxide was diluted with water and titrated against a primary standard (potassium biphthalate) using phenolphthalein as an indicator.

Tetrahydrofuran (THF)

Reagent grade THF was fractionally distilled over lithium aluminum hydride and stored in a dark bottle under nitrogen.[178]

PURIFICATION AND FUNCTIONALIZATION OF THE POLYMER SUPPORT

Polystyrene (1)

Both the Amberlite XE-305 and Biobead SM-16 (100 g each) were washed before use with 1 L volumes of the solvents employed by Farrall and Fréchet.[111] The resins were finally rinsed in a Soxhlet apparatus with ether, then hexane, for 12 hr each before being dried under reduced pressure at 60 °C.[74]

Polymer-supported Benzyl Chloride (2)

Chloromethylated polystyrene (**2**) was prepared, from both the Amberlite and SM-16 resins, according to the method of Hodge and Sherrington.[93a] Elemental analysis (Table 3) and FTIR data are given in the text.

Polymer-supported Benzyl Iodide (3)

The iodomethylated polystyrene (**3**) was prepared from chloromethylated resin **2** according to reported methods[92] as outlined by Bovee.[75] The FTIR and elemental analysis data (Table 3) are given in the text. The high resolution ^{13}C-NMR spectrum of **3** (Fig. 8A) showed signals for the polystyrene backbone (**P**) that

were consistent with the spectra reported by Ford et al.[132-134] However, no signal for the benzyl iodide carbon was evident. A signal (46 ppm)[132-134] for the benzylic carbon of the chloromethylated precursor (PBnCl) was also absent, thus confirming the FTIR and elemental analysis data which showed that the chloride units had been quantitatively displaced.

Polymer-supported Trityl Chloride (14)

Polymer-supported trityl chloride (**14**), and its precursors, brominated Amberlite XE-305 (**11**) and polymer-supported trityl alcohol (**13**), were prepared according to the general method of Farrall and Fréchet[111] as described by Apfeld.[74] The trityl alcohol was treated twice with acetyl chloride to extend the conversion of hydroxyl to chloride groups as discussed in the text. The elemental analysis data are presented in Table 4.

SYNTHESIS OF COMPOUNDS

Polymer-supported Phenol System

Syringyl alcohol (**72**), disyringylmethane (**73**), and bisyringyl (**74**), were prepared as described by Smith.[18] A sample of guaiacylpropane (3-methoxy-4-hydroxyphenylpropane, **4**), prepared from the catalytic hydrogenation of eugenol (**23**), was donated by Dr. P. Apfeld.[74]

3-(3'-Methoxy-4'-hydroxyphenyl)propan-1-ol (15)

Guaiacylpropanol was prepared as described by Apfeld and Dimmel.[180] After vacuum distillation, the purified material crystallized on standing to give a white solid: mp 164-165 °C.

Polymer-supported Trityl Ether Linked Guaiacylpropanol (5)

Under anhydrous conditions, the polymer-supported trityl chloride **14** (5.05 g, 2.7 mmol Cl) was slurried with 3.0 g (17 mmol) of guaiacylpropanol (**15**) at 45-50 °C in 75 mL of a benzene/pyridine (1:2) solvent mixture. Stirring, with a small stirring bar as described by Apfeld,[74] was maintained for six days after which the reaction mixture was allowed to cool. The resin was isolated by filtration and washed with 3x50 mL aliquots of pyridine and benzene. The resin was then extracted in a Soxhlet apparatus with ether and hexane for 10-12 hr each. The product was finally dried under vacuum at 45 °C. The elemental and methoxyl analysis data are presented in Table 4.

1-Allyl-3-methoxy-4-methoxyethoxymethoxybenzene (24)[126]

Sodium hydride (3.82 g, 15.8 mmol) was slurried under anhydrous conditions in 150 mL of THF. The mixture was cooled to 0 °C before slowly adding 20.0 g (12.2 mmol) of eugenol (**23**) dissolved in 50 mL of THF. Stirring was maintained for 30 min at 0 °C before the dropwise addition of 24.9 g (20.1 mmol) of cold MEM chloride. The resulting solution was stirred for 30 min at 0 °C and then warmed to room

temperature. The reaction was quenched after stirring an additional 2 hr by carefully adding 100 mL of water. The aqueous and organic phases were separated and the aqueous phase extracted (2x50 mL) with ether. The extract was combined with the initial organic layer which was then washed with 2x50 mL of 0.1M NaOH followed by 50 mL of a sat. sodium chloride solution. The product mixture was dried over sodium sulfate (Na_2SO_4) and filtered. The solvent was removed from the filtrate under reduced pressure yielding 31.2 g of a yellowish oil. Purification by column chromatography (eluent: chloroform) yielded 29.3 g (95%) of a white oil: IR (cm^{-1}) 1640 ($CH=CH_2$), 1100, 1000 (C-O), 950, 915 (C=C-H); ^{1}H-NMR ($CDCl_3$) δ 3.33 (d, 2, J = 6.8 Hz, $ArCH_2$), 3.36 (s, 3, $ROCH_3$), 3.50-3.60 (m, 2, $OCH_2\underline{CH_2}O$), 3.85 (s, 3, $ArOCH_3$), 3.87 (m, 2, $O\underline{CH_2}CH_2O$), 4.99-5.17 (m, 2, $=CH_2$), 5.28 (s, 2, OCH_2O), 5.76-6.16 (d of d of t, 1, J = 17, 11, and 9 Hz, CH=), 6.68 (d of d, 1, J = 6.4 and 2.0 Hz, C_5-H), 6.73 (s, 1, C_2-H), 7.11 (d of d, 1, J = 6.1 and 2.7 Hz, C_6-H); ^{13}C-NMR ($CDCl_3$) ppm 39.8 (t, $ArCH_2$), 55.7 (q, $ArOCH_3$), 59.5 (q, $ROCH_3$), 67.6 (t, $OCH_2\underline{CH_2}O$), 71.4 (t, $O\underline{CH_2}CH_2O$), 94.5 (t, OCH_2O), 112.2 (d, C_2), 115.4 (t, $=CH_2$), 116.7 (d, C_5), 120.4 (d, C_6), 134.2 (s, C_1), 137.2 (d, CH=), 144.6 (s, C_4), 149.3 (s, C_3); MS z/e (relative intensity) 252 (31, M^+), 164 (13), 89 (100), 59 (65).

3-(3'-Methoxy-4'-methoxyethoxymethoxyphenyl)propan-1-ol (22)

Under anhydrous conditions, a solution of 200 mL of cold 0.5M disiamylborane in THF (prepared freshly from a kit supplied by Aldrich Chemical Co.) was slowly added with stirring to 6.3 g (25 mmol) of eugenol-MEM (**24**) in 50 mL of THF

cooled to 0 °C. The residual borane complex was decomposed by the careful addition of 45 mL of water after stirring for 3 hr at 0 °C. Sodium hydroxide (3M, 450 mmol) was then added to the reaction solution following which hydrogen peroxide (30% solution, 1.1 mol) was slowly dripped in. The resulting mixture was stirred for 30 min at room temperature. Potassium carbonate was then added until the aqueous layer became saturated. The THF layer was removed and the aqueous layer extracted with additional THF (4x50 mL). The combined THF solution was dried over Na_2SO_4 and filtered. An average of 10.5 g of crude product was obtained after removing the solvent under reduced pressure. A colorless oil (6.11 g, 90%) was obtained after purification on a silica gel column (eluent: 2-3% methanol/dichloromethane): IR (cm^{-1}) 3600-3100 (OH), 1100, 990 (C-O), no $CH=CH_2$ signals were observed; ^{1}H-NMR ($CDCl_3$) δ 1.71 (s, 1, ROH, exchangeable in D_2O), 1.88 (m, 2, β-CH_2), 2.65 (d of d, 2, J = 8.9 and 6.5 Hz, $ArCH_2$), 3.36 (s, 3, $ROCH_3$), 3.46-3.73 (m, 4, $O\underline{CH_2CH_2}O$), 3.82 (m, 2, CH_2OH), 3.85 (s, 3, $ArOCH_3$), 5.27 (s, 2, OCH_2O), 6.69 (d of d, 1, J = 7 and 2.0 Hz, $C_{5'}$-H), 6.74 (s, 1, $C_{2'}$-H), 7.09 (d of d, 1, J = 7.0 and 1.6 Hz, $C_{6'}$-H); ^{13}C-NMR ($CDCl_3$) ppm 31.6 (t, $ArCH_2$), 34.2 (t, β-CH_2), 55.5 (q, $ArOCH_3$), 58.7 (q, $ROCH_3$), 61.8 (t, CH_2OH), 67.5 (t, $OCH_2\underline{CH_2}O$), 71.3 (t, $O\underline{CH_2}CH_2O$), 94.5 (t, OCH_2O), 112.0 (d, $C_{2'}$), 116.6 (d, $C_{5'}$), 120.2 (d, $C_{6'}$), 136.2 (s, $C_{1'}$), 144.2 (s, $C_{4'}$), 149.3 (s, $C_{3'}$); MS z/e (rel. int.) 270 (22, M^+), 194 (12), 138 (14), 137 (28) 89 (97), 59 (100).

3-(3'-Methoxy-4'-allyloxyphenyl)propan-1-ol (25)

Guaiacylpropanol (**15**) (15.8 g, 86.8 mmoles) was dissolved in 100 mL of a 50% (v/v) solution of benzene/DMF and added dropwise to a stirring mixture of NaH (2.15 g, 86.8 mmoles) in 50 mL of benzene. After 30 min, 15.0 mL (174 mmoles) of distilled allyl bromide in 150 mL of benzene was dripped into the reaction vessel. Stirring was maintained for 10 hr after which 100 mL of 1M sodium methoxide was slowly added. After stirring for an additional 30 min, the reaction mixture was diluted with 50 mL of water and the resulting layers were separated. The organic layer was washed repeatedly with water. The aqueous washes were combined with the initial aqueous phase and then acidified with 6M HCl. The acidic solution was extracted with chloroform ($CHCl_3$). The $CHCl_3$ extracts were combined with the initial organic layer and dried over Na_2SO_4. The solvent was evaporated under reduced pressure (water aspirator), followed by evaporation under high vacuum, to remove the residual DMF. The crude product was purified by column chromatography (eluent: 25% to 75% ethyl acetate/toluene) yielding 18.2 g (94%) of a light gold oil: IR (cm^{-1}) 3600-3100 (OH), 995, 910 (C=C-H); ^{1}H-NMR ($CDCl_3$) δ 1.60 (s, 1, ROH, exchangeable in D_2O), 1.79 (m, 2, β-CH_2), 2.64 (d of d, 2, J = 8.7 and 6.5 Hz, $ArCH_2$), 3.66 (t, 2, J = 6.5 Hz, CH_2OH), 3.85 (s, 3, OCH_3), 4.57 (d of t, 2, J = 5.4 and 1.5 Hz, $ArOCH_2$), 5.18-5.48 (d of d of q, 2, J = 16.5, 9.3, and 1.5 Hz, $=CH_2$), 5.89-6.27 (d of d of t, 1, J = 16.5, 9.3, and 1.5 Hz, CH=), 6.65-6.85 (m, 3, Ar-H); ^{13}C-NMR ($CDCl_3$) ppm 31.6 (t, $ArCH_2$), 34.2 (t, β-CH_2), 55.8 (q, OCH_3), 61.9 (t, CH_2OH), 70.0 (t, $ArOCH_2$), 112.2 (d, $C_{2'}$), 113.7 (d, $C_{5'}$), 117.4 (t, $=CH_2$), 120.0 (d, $C_{6'}$), 133.4 (s, $C_{1'}$), 134.8 (d, CH=), 145.9 (s, $C_{4'}$),

149.1 (s, $C_{3'}$); MS z/e (rel. int.) 222 (68, M^+), 181 (72), 164 (12), 163 (100), 137 (18), 135 (17), 121 (10), 107 (43), 105 (17), 103 (27), 91 (28), 79 (18), 78 (11), 77 (24), 65 (11), 41 (11), 39 (11).

Anal. calcd. for $C_{13}H_{18}O_3$ (%): C, 70.2; H, 8.2; O, 21.6. Found: C, 70.5; H, 8.1; O, 21.6.

1-Benzyloxy-3-(3'-methoxy-4'-allyloxyphenyl)propane (26)

To a stirring mixture of 0.33 g (14 mmoles) of NaH in 15 mL of DMF was added, via a dropping funnel, 2.00 g (9.00 mmoles) of allyl-protected guaiacyl-propanol (**25**) dissolved in 20 mL DMF. After the reaction mixture had stirred for 1 hr, 4.28 mL (36.0 mmol) of benzyl bromide was added: Stirring continued for 5 days, after which methanol (20 mL) was slowly added, followed by 40 mL of water. The resulting solution was extracted with $CHCl_3$ which was subsequently removed under reduced pressure. Residual DMF was evaporated from the remaining organic phase under high vacuum. The crude product was purified by column chromatography (eluent: dichloromethane) yielding 1.81 g (64%) of a light yellow oil: IR (cm^{-1}) OH signal absent; ^{1}H-NMR (d_6-DMSO) δ 1.68-1.96 (m, 2, β-CH_2), 2.57 (d of d, 2, J = 8.3 and 6.5 Hz, ArCH_2), 3.43 (t, 2, J = 6.4 Hz, CH_2OBn), 3.73 (s, 3, OCH_3), 4.45-4.52 (m, 4, BnCH_2O, ArOCH_2), 5.13-5.46 (d of d of q, 2, J = 17.3, 10.3, and 1.5 Hz, =CH_2), 5.84-6.22 (d of d of t, 1, J = 17.3, 10.3 and 1.5 Hz, CH=), 6.60-6.88 (m, 3, Ar-H), 7.32 (s, 5, Ar-H of benzyl); ^{13}C-NMR (d_6-DMSO) ppm 31.0 (t, ArCH_2), 31.3 (t, β-CH_2), 55.4 (q, OCH_3), 68.9 (t, CH_2OH), 69.2 (t, ArOCH_2), 71.7 (t, BnCH_2O), 112.5 (d, $C_{2'}$), 113.9 (d, $C_{5'}$), 116.7

(t, $=CH_2$), 119.8 (d, $C_{6'}$), 126.9 (d, C_4 of benzyl), 127.0 (d, $C_{3,5}$ of benzyl), 127.8 (d, $C_{2,6}$ of benzyl), 133.8 (s, $C_{1'}$), 134.5 (d, CH=), 138.4 (s, C_1 of benzyl), 145.6 (s, $C_{4'}$), 148.9 (s, $C_{3'}$); MS z/e (rel. int.) 312 (20, M^+), 221 (5), 177 (5), 137 (7), 92 (8), 91 (100), 77 (5), 65 (6).

1-Benzyloxy-3-(3'-methoxy-4'-hydroxyphenyl)propane (18)

In 50 mL of an ethanol/benzene/water (7:3:1 v/v) mixture was dissolved 0.51 g (15 eq.) of the starting compound (**26**) along with catalytic amounts (0.10 g, 1 eq.) of tris(triphenylphosphine)rhodium(I) chloride (TTPPR) and 0.05 g (4 eq.) of 1,4-diazo-bicyclo[2.2.2]octane (Dabco).[128, 129] The mixture was refluxed for 24 hr and then cooled. Water (25 mL) was added and the reaction mixture extracted with $CHCl_3$. The extracts were concentrated under reduced pressure and then dissolved in 60 mL of acetone/1M HCl (9:1 v/v). After refluxing for 1.5 hr, the reaction mixture was cooled, diluted with 50 mL of water, and extracted with $CHCl_3$. The combined $CHCl_3$ extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. A GLC analysis of the product mixture indicated that the allyl deprotection was incomplete. The two procedures were repeated to achieve complete conversion. The crude product, a dark oil, was purified by column chromatography (eluent: 10% ethyl acetate/toluene) yielding a light yellow oil: MS z/e (rel. int.): 272 (71, M^+), 181 (40), 164 (27), 151 (49), 137 (100), 122 (13), 119 (23), 119 (23), 91 (77), 77 (18), 65 (15).

Polymer-supported 4-O-Allylguaiacylpropanol (27)

Allyl-protected guaiacylpropanol (**25**) (4.25 g, 19.1 mmoles) was dissolved in 50 mL of THF and added dropwise to 0.46 g (18.9 mmoles) of NaH slurried in 25 mL of THF. The resulting mixture was stirred (overhead) for 60 min. Polymer-bound benzyl iodide (**3**) (6.00 g, 14.7 mmoles) was then added to the reaction flask. Stirring continued for 114 hr, after which the resin was isolated in two batches by filtration and washed with 3x200 mL of THF each. The resin was further washed in a Soxhlet apparatus with THF followed by hexane for 12 and 11 hr, respectively. A yield of 7.03 g of coupled material (**27**) was obtained after the resin had dried in vacuo at 40 °C. Reported yields are approximate values due to static losses on transferring operations. The FTIR spectrum of **27** exhibited signals assigned to the bound guaiacylpropanol appendage at 1262 and 1229 (Ar-O-R), 1141 and 1101 (R-O-R), and at 997 and 926 (C=C-H) cm^{-1}. Signals at 1512 (Ar C=C) and 1419 ($-CH_2-$) cm^{-1}, which were also attributed to the bound model, were enhanced relative to those observed in the spectrum of the precursor benzyl iodide (**3**). The elemental analysis data (Table 6) for compounds **27**, **28**, and **6** are discussed in the text.

A sample of the reaction liquor was taken to dryness under reduced pressure. The residue was dissolved in $CHCl_3$, diluted with an equal volume of water, and acidified with 6M HCl. The organic layer was separated, washed with water, dried (Na_2SO_4), and concentrated under vacuum. A GLC analysis of the resulting

solution revealed the presence of unmodified soluble model (**25**), thus confirming that the allyl group is stable under the specified coupling reaction conditions.

Polymer-supported 4-O-Allylguaiacylpropanol/Ethoxide (28)

The unreacted benzyl iodide units from the coupling reaction were converted into nonreactive benzyl ethoxide groups. The coupled material (**27**) (6.75 g) was slurried under nitrogen in 35 mL of THF to which an excess (165 mL) of 0.8M sodium ethoxide in ethanol was added. The reaction mixture was stirred for 103 hr after which the resin was isolated by filtration. Washings were conducted with 6x100 mL portions of methanol, acetone, and THF. The resin product (**28**) was dried at 40 °C under reduced pressure, after being rinsed in a Soxhlet apparatus with hexane for 6.5 hr. A yield of 6.37 g was isolated. The polystyrene backbone signals in the high resolution ^{13}C-NMR spectrum of **28** were weak (Fig. 8C) but remained consistent with those reported by Ford.[132-134] The benzyl ethoxide signals (15.8 ppm, $BnOCH_2\underline{C}H_3$; and 65.6 ppm, $BnO\underline{C}H_2CH_3$) were also weak relative to the signals from the supported model. Weak benzyl ethoxide signals are consistent with the FTIR and elemental analysis data which indicated that the ethoxide loading was low due to an initially high displacement of iodide groups during the coupling reaction. Broad signals due to the supported model were observed as follows: ($CDCl_3$) ppm 31.8 ($ArCH_2$ and β-CH_2), 55.9 (OCH_3), 70.0 (PCH_2O, CH_2OBnP, and $ArOCH_2$), 113.5 (C_2 and C_5), 117.7 (=CH_2), 120.6 (C_6), 133.8 (C_1 and CH=), 150.3 (C_4 and C_3).

Polymer-supported Guaiacylpropanol/Ethoxide (6)

The allyl protecting group was removed from the phenolic site of the bound model as follows. Tris(triphenylphosphine)rhodium(I) chloride (1.15 g, 1.25 mmoles) and 0.51 g (0.45 mmoles) of Dabco were dissolved in 275 mL of a warm ethanol/benzene/water (7:3:1 v/v) solution. The ethoxide treated resin **28** (5.38 g) was added and the reaction mixture gently refluxed for 9.5 hr. Once cool, the resin was isolated by filtration and washed (5x100 mL) with $CHCl_3$, THF, and hexane before being dried under reduced pressure at 40 °C. The resin, which now supported the isomerized protecting group, was suspended in a mixture of 1.2M HCl (35 mL) and acetone (175 mL). After gently refluxing for 4 hr, the reaction mixture was allowed to cool. The resin was filtered and washed (5x100 mL) with acetone, THF, and hexane. The allyl deprotection sequence was repeated twice more. On the third trial, the acid reflux was extended to 6 hr. The final product was washed in a Soxhlet apparatus for 6 hr with hexane before being dried in a vacuum oven at 40 °C. The isolated yield of **6** was 4.86 g. High resolution ^{13}C-NMR signals for supported model **6** (Fig. 8D) were observed as follows: ($CDCl_3$) ppm 31.8 ($ArCH_2$ and β-CH_2), 55.8 (OCH_3), 70.0 (PCH_2O and CH_2OBnP), 111.2 (C_2), 114.3 (C_5), 121.0 (C_6), 133.8 (C_1), 143.8 (C_4), 146.6 (C_3). The signals at 70.0 ($ArOCH_2$), 117.8 ($=CH_2$), and 133.8 (CH=) were greatly reduced in relative area (vs. the spectrum of **28**) indicating that a substantial portion of the allyl groups were removed.

Polymer-supported Benzyl Ethoxide

Under a continuous stream of nitrogen, 2.50 g (6.13 mmol) of dried polymer-bound benzyl iodide (**3**) was stirred (overhead) for 112 hr in 16 mL of freshly distilled THF and an excess (64 mL) of 0.9M sodium ethoxide in ethanol. The reacted resin was isolated by filtration and washed with 6x50 mL of methanol, acetone, and THF. The product was then extracted with hexane for 8 hr and dried under reduced pressure at 40 °C. Elemental analysis showed a residual iodide content of 0.21 mmol/g. To reduce the level of remaining iodide, a second ethoxide treatment was conducted for 76 hr in an analogous manner. The FTIR spectrum of the final product showed a strong signal at 1098 cm^{-1} (C-O str.) in place of the original benzyl iodide signal at 1155 cm^{-1}. Elemental analysis gave the following: C, 82.1; H, 8.3; O, 8.7; I, 1.1 (0.09 mmol of iodide per gram of resin). The ensuing assignments were made for the observed signals in the high resolution ^{13}C-NMR spectrum (Fig. 8B) of the polymer-bound benzyl ethoxide: ^{13}C-NMR ($CDCl_3$) ppm 15.4 (CH_3), 40.5 (backbone methine),[132-134] 38-47 (backbone methylene), 65.6 (OCH_2), 72.8 ($ArCH_2O$), 126.5 (C_4), 128.3 ($C_{2,3,5,6}$), 146.2 (C_1).

Polymer-supported Benzyl Propoxide

Sodium propoxide was prepared by dissolving freshly cut sodium metal in propanol under a nitrogen atmosphere. Polymer-supported propoxide was prepared by stirring 1.00 g (3.09 mmoles) of polymer-bound benzyl iodide (**3**) in 40 mL of 1M sodium propoxide in propanol and 15 mL of dry DMF for three days. The resin was

isolated by filtration and washed successively with methanol and acetone (4x100 mL) followed by THF and hexane (3x100 mL). The washed resin was dried in a vacuum oven at 40 °C. An aliphatic ether stretch signal at 1097 cm^{-1} was observed in the FTIR spectrum along with additional C-H stretch signals at 2961 and 2878 cm^{-1}. An iodine loading of 0.35 mmol/g remained on the resin; a methoxyl content of 7.81% was also observed. The positive test for methoxyl units confirms that the propoxide group, and the allyl group as shown below, interfere with the methoxyl determination.

Polymer-supported Benzyl Allyloxide

The polymer-supported allyloxide was prepared in an analogous manner to the heterogeneous propoxide. The FTIR spectrum showed characteristic signals at 1097 (C-O), 991 and 923 (C=C-H) cm^{-1}. The resin had a methoxyl content of 5.73%.

2,4'-Dihydroxy-5-propyl-3,3',5'-trimethoxydiphenylmethane (8)

Guaiacylpropane (**4**) (1.00 g, 6.02 mmol) and syringyl alcohol (**72**) (2.22 g, 12.05 mmol) were heated under a nitrogen atmosphere for 18 hr at 138 °C in 200 mL of 2M NaOH. The reaction vessel has been described elsewhere.[181] The cooled reaction mixture was acidified to pH 2 with 5M sulfuric acid and then extracted repeatedly with $CHCl_3$. The combined $CHCl_3$ extracts were reduced in volume to give a brownish oil which was purified by column chromatography (eluent: 30% hexane/chloroform followed by a 15% solvent mixture). The fractions containing **8**, as determined

by GLC, were combined and concentrated. The resulting yellowish oil was recrystallized in toluene/pet. ether to give 0.20 g (20% yield) of a white solid: mp, 74.5-76.2 °C, ^{1}H-NMR ($CDCl_3$) δ 0.90 (t, 3, J = 7.5 Hz, CH_3), 1.57 (sextet, 2, J = 7.3 Hz, β-CH_2), 2.47 (unresolved d of d, 2, ArCH_2), 3.82 (s, 6, OCH_3'), 3.85 (s, 3, OCH_3), 3.88 (s, 2, Ar_2CH_2), 5.37, 5.59 (2 s, 2, ArOH, exchangeable in D_2O), 6.49 (s, 2, $C_{2',6'}$-H, and unresolved doublet, 1, C_4-H), 6.57 (d, 1, J = 1.7 Hz, C_6-H); ^{13}C-NMR ($CDCl_3$) ppm 13.8 (q, CH_3), 24.9 (t, β-CH_2), 35.6 (t, Ar_2CH_2), 37.7 (t, ArCH_2), 55.9 (q, OCH_3), 56.2 (q, OCH_3'), 105.6 (d, $C_{2',6'}$), 108.8 (d, C_4), 122.0 (d, C_6), 126.4 (s, C_1), 131.8 (s, $C_{4'}$), 132.8 (s, C_2), 133.5 (s, $C_{1'}$), 141.0 (s, C_5), 145.9 (s, C_3), 146.6 (s, $C_{3',5'}$); MS z/e (rel. int.) 332 (55, M^+), 257 (15), 179 (40), 178 (41), 154 (100), 149 (39), 139 (14), 115 (16), 91 (16), 77 (17).

Anal. calcd. for $C_{19}H_{24}O_5$ (%): C, 68.7; H, 7.3; O, 24.1. Found: C, 68.5; H, 7.3; O, 24.2.

2,4'-Dihydroxy-5-propan-3''-ol-3,3',5'-trimethoxydiphenylmethane (77)

A solution of 1.96 mmolar syringyl alcohol (**72**) in 1.0M NaOH (reagent grade) was prepared under nitrogen. The solution was then added (55 mL per bomb) to each of four 70 mL capacity titanium reaction vessels (bombs) containing 100 mg of polymer-bound guaiacylpropanol (**6**). The bombs were rotated at 170 °C for 3 hr and then cooled. The reaction mixture was filtered and the collected beads washed with 4x50 mL of the solvents described later for the heterogeneous benzyl ether stability test, and dried in a vacuum oven at 40 °C. The supported lignin model (**6**) was subjected to the condensation procedure a total of three times.

The ITS method,* employing the following quantities, was used to cleave reacted and unreacted starting material from the resin: 340 mg of reacted resin, 15 mL of dry acetonitrile, 0.68 mL of ITS, 10 mL of anhydrous methyl alcohol, and 4.25 mL of pyridine. The liquor from the beads, along with 5x10 mL methanol rinses of the resin, were concentrated under pressure at a maximum of 40 °C. The residue was stirred in 10 mL of water and then extracted with 3x10 mL of dichloromethane (CH_2Cl_2). The organic extract was dried over Na_2SO_4 and then concentrated to a dark oil (0.101 g). The oil was purified by column chromatography, employing first 10:1, 8:1, and 6:1 dichloromethane/ethyl acetate mixtures, and finally a 5% methanol/dichloromethane solution. A second chromatography of select coeluted fractions, with a 3% methanol/dichloromethane solution as the eluent, gave only 8 mg of **77**, as a yellow solid: ^{1}H-NMR ($CDCl_3$) δ 1.83 (pentet, 3, J = 7.7 Hz, β-CH_2, also contains a D_2O exchangeable OH proton), 2.59 (t, 2, J = 6.4 Hz, ArCH_2), 3.65 (t, 2, J = 7.0 Hz, CH_2O), 3.84 (s, 6, OCH_3'), 3.87 (s, 3, OCH_3), 3.88 (s, 2, Ar_2CH_2), 5.37, 5.60 (2 s, 2, ArOH, exchangeable in D_2O), 6.49 (s, 2, $C_{2',6'}$-H), 6.52 (d, 1, J = 1.6 Hz, C_4-H), 6.59 (d, 1, J = 1.8 Hz, C_6-H); ^{13}C-NMR ($CDCl_3$) ppm 31.9 (t, ArCH_2), 34.5 (t, β-CH_2), 35.6 (t, Ar_2CH_2), 56.0 (q, OCH_3), 56.5 (q, OCH_3'), 62.2 (t, CH_2OH), 105.7 (d, $C_{2',6'}$), 109.0 (d, C_4), 122.2 (d, C_6), 126.8 (s, C_1), 131.9 (s, $C_{4'}$), 132.9 (s, C_2), 141.4 (s, C_5), 146.3 (s, C_3), 146.9 (s, $C_{3',5'}$), a signal for $C_{1'}$ was not observed; MS z/e (rel. int.) 348 (72, M^+), 195 (25), 194

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* For further details see the section entitled "LOADING CHARACTERIZATION OF THE SUPPORTED MODELS".

(11), 167 (18), 154 (100), 150 (60), 149 (15), 121(12). The NMR spectra of **77** were performed by Spectral Data Services.[177]

3,4,5-Trimethoxybenzylmethyl Ether

Excess dimethylsulfate (23.9 mL, 253 mmol) was added after 1 hr to a stirring mixture of 3,4,5-trimethoxybenzyl alcohol (10.0 g, 50.5 mmol) in 100 mL of 1M NaOH at 50 °C. Stirring was maintained for 30 min before the reaction was quenched with the addition of 108 mL of concd. ammonium hydroxide. After an additional 30 min, the mixture was cooled and extracted with 3x20 mL of $CHCl_3$. The combined extracts were reduced in volume and resubjected to the above methylation conditions. Purification of the resulting oil was attained by successive fractional distillations. A final yield of 1.05 g (10%) of a colorless oil was realized: bp 143-146 at < 10 mm Hg; ^{1}H-NMR ($CDCl_3$) δ 3.40 (s, 3, $CH_2O\underline{CH_3}$), 3.83 (s, 3, C_4OCH_3), 3.86 (s, 6, $C_{3,5}OCH_3$), 4.39 (s, 2, $ArCH_2$), 6.57 (s, 2, $C_{2,6}$-H); ^{13}C-NMR ($CDCl_3$) ppm 53.9-62.5 (m, OCH_3), 74.6 (t, $ArCH_2$), 104.3 (d, $C_{2,6}$), 133.6 (s, C_1), 137. 1 (s, C_4), 152.9 (s, $C_{3,5}$); MS z/e (rel. int.) 212 (78, M^+), 197 (14), 182 (51), 181 (100), 169 (35), 139 (32), 138 (39). This material was employed as a GLC response factor standard for quantifying the syringyl alcohol (**72**) remaining in the high temperature reaction product mixtures.

Polymer-supported Quinone Methide System

α-Hexoxy-3-methoxy-4-allyloxy-6'-hydroxyacetophenone (36)

Under anhydrous conditions, 1,6-hexanediol (68.9 g, 583 mmol) dissolved in 350 mL of DMF, was added to a stirring (overhead) mixture of NaH (12.4 g, 500 mmol) in 300 mL of DMF at 50 °C. After 30 min, bromoketone **52** (24.1 g, 83.3 mmol) in 150 mL of DMF was dripped into the stirring reaction mixture. The reaction proceeded for 90 min after which 100 mL of water was carefully added. The resulting solution was then poured into 1.5 L of ice-water, acidified to pH 3 with 6M HCl, and extracted with $CHCl_3$ (6x200 mL). The organic extract was washed with water (8x250 mL), dried (Na_2SO_4), and reduced in volume. The residual DMF was removed via distillation under high vacuum after the addition of 200 mL of xylenes.[163] The crude product was dissolved in CH_2Cl_2 (100 mL), washed again with water (4x100 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The residual material was dissolved in 20 mL of CH_2Cl_2 and filtered yielding 7.38 g of a yellow solid which was recrystallized in toluene followed by ethyl acetate. Additional product was obtained from the above filtrate. A final yield of 10.7 g (45%) of α-hexoxy-3-methoxy-4,6'-dihydroxyacetophenone, a reddish solid, was obtained: mp 116.5-118; IR (cm^{-1}) 3500-3300 (OH), 1680 (C=O), 1240 (Ar-O), 1150, 1130 (C-O); ^{1}H-NMR (d_6-DMSO) δ 1.33-1.60 (m, 8, $(CH_2)_4$), 3.33-3.53 (m, 5, O$\underline{CH_2}$ and $\underline{CH_2}$OH, one proton exchangeable in D_2O), 3.90 (s, 3, OCH_3), 4.68 (s, 2, $COCH_2$), 6.86 (d of d, 1, J = 7.2 and 1.3 Hz, C_5-H), 7.44 (s, 1, C_2-H), 7.48 (d of d, 1, J = 7.3 and 1.8 Hz, C_6-H), the

aromatic hydroxyl proton was not readily discernible; ^{13}C-NMR (d_6-DMSO) ppm 25.4 (t, $C_{4'}$), 25.6 (t, $C_{3'}$), 29.4 (t, $C_{2'}$), 32.6 (t, $C_{5'}$), 55.7 (q, OCH_3), 60.8 (t, $C_{6'}$), 70.7 (t, $C_{1'}$), 73.0 (t, $CO\underline{CH_2}$), 113.1 (d, C_2), 114.9 (d, C_5), 122.6 (d, C_6), 126.7 (s, C_1), 147.4 (s, C_4), 151.7 (s, C_3), 194.5 (s, C=O); MS (DIP) z/e (rel. int.) 282 (1, M^+), 166 (23), 151 (100).

Next, the phenolic hydroxyl group of the dihydroxyacetophenone intermediate was protected as an allyl ether. Under anhydrous conditions, 6.00 g (21.3 mmol) of the dihydroxy compound was slurried with NaH (0.53 g, 21.3 mmol) in 500 mL of DMF at 60 °C. After 2 hr, 3 eq. of allyl bromide (5.53 mL, 63.9 mmol) were added to the stirring reaction mixture. Stirring was maintained at 60 °C for 48 hr after which 100 mL of water followed by 500 mL of ice-water were added. The chilled reaction mixture was extracted with $CHCl_3$, washed with water (3x100 mL), and dried over Na_2SO_4. The solvent was removed under reduced pressure followed by high vacuum as previously detailed. An orange oil (5.78 g, 84%) was obtained after purification by column chromatography (eluent: 2 to 6% methanol/dichloromethane). The oil was eventually recrystallized in toluene: mp 70-72 °C; IR (cm^{-1}) 995, 925 (C=C-H); ^{1}H-NMR ($CDCl_3$) δ 1.40-1.73 (m, 8, $(CH_2)_4$ and ROH, exchangeable in D_2O), 3.56, 3.62 (2 t, 4, J = 6.4 Hz, $O\underline{CH_2}CH_2$ and CH_2OH), 3.92 (s, 3, OCH_3), 4.66-4.72 (m, 4, $COCH_2$ and $ArOCH_2$), 5.25-5.52 (d of d of q, 2, J = 18.8, 10.3, and 1.5 Hz, $=CH_2$), 5.89-6.22 (d of d of t, 1, J = 18.8, 10.3, and 1.5 Hz, CH=), 6.83-6.92 (m, 1, C_5-H), 7.49-7.60 (m, 2, $C_{2,6}$-H); ^{13}C-NMR ($CDCl_3$) ppm 25.2 (t, $C_{4'}$), 25.5 (t, $C_{3'}$), 29.3 (t, $C_{2'}$), 32.3 (t, $C_{5'}$), 55.6 (q, OCH_3), 62.0 (t, $C_{6'}$), 69.2 (t, $ArOCH_2$), 71.2 (t, $C_{1'}$), 73.2 (t, $CO\underline{CH_2}$), 110.2 (d, C_2),

111.4 (d, C_5), 117.8 (t, $=CH_2$), 121.9 (d, C_6), 127.7 (s, C_1), 132.9 (d, CH=), 148.8 (s, C_4), 152.0 (s, C_3), 194.5 (s, C=O); MS z/e (rel. int.) 322 (3, M^+), 206 (22), 191 (100), 103 (6).

Benzylation of the Substituted Acetophenone 36

Substituted acetophenone **36** (1.01 g, 3.12 mmol) was deprotonated with 1.4 eq. of NaH in the usual manner and treated with 3 eq. of benzyl iodide (Kodak) in DMF at 60 °C for 48 hr. The product work-up and isolation were analogous to that employed when protecting **36** with the allyl group. The MS, z/e (rel. int.), for the benzylated product is as follows: 412 (2, M^+), 296 (33), 294 (11), 249 (15), 191 (100), 129 (14), 121 (23), 120 (11), 103 (19), 101 (34), 91 (20), 83 (64), 55 (22).

The molecular ion (M^+) in the MS shows, by an increase of 90 mass units, that starting material **36** was benzylated. However, a signal at 296, which corresponds to a loss of 116 mass units, suggests that the recipient of the benzyl group was not the primary hydroxyl on the hexanol spacer chain as desired. The loss of 116 units was prevalent in both the MS of **36** and its unprotected precursor as reported above. The mass reduction is consistent with a standard McLafferty-type rearrangement in which the hexanol side chain (O-$(CH_2)_6$-O) is cleaved.[182, 183] The persistent M-116 signal led to the speculation that the benzyl group had been added at the α-carbon (**40**).

The benzylated product was analyzed by ^{1}H-NMR to confirm the position of the benzylation site. The spectrum obtained was of rather poor quality,[184] but

generally corresponded to proposed structure 40; it was clearly evident that the primary hydroxyl group had not been derivatized.[182]

6-(2'-(1",3"-Dioxolane)-2'-(3'"-methoxy-4'"-allyloxyphenyl))ethoxyhexan-1-ol (41)

Initially, 1.70 g (6.02 mmol) of α-hexoxy-3-methoxy-4,6'-dihyroxyaceto-phenone was refluxed for 22 hr with 0.57 g (3.00 mmol) of p-toluene sulfonic acid monohydrate and an excess (30.1 mmol) of ethylene glycol in 175 mL of benzene and 50 mL of THF.[158] The reaction liquor was cooled and poured into 200 mL of ice-water. The layers were then separated and the aqueous layer extracted with $CHCl_3$. The $CHCl_3$ extract was combined with the original organic phase, dried (Na_2SO_4), and concentrated. The crude material was purified by column chromatography (eluent: 4% methanol/dichloromethane). The intermediate product, 6-(2'-(1",3"-dioxolane)-2'-(3'"-methoxy-4'"-hydroxyphenyl))ethoxyhexan-1-ol, a gold-colored oil, was obtained in a 60% yield: MS z/e (rel. int.) 326 (0.1, M^+), 195 (100), 151 (20).

Under anhydrous conditions, the dioxolane intermediate (0.97 g, 2.97 mmol) was dissolved in 20 mL of a THF/benzene (3:1) solution and added dropwise to 1 eq. of NaH stirring in benzene. After 30 min, the mixture was warmed to 50 °C. Two e-quivalents of allyl bromide in 10 mL of benzene were then added. Due to rapid sol-vent evaporation, DMF was added to maintain the liquor volume. The reaction was quenched with 10 mL of 1M sodium methoxide in methanol after 26 hr at 43 °C. The reaction mixture was stirred an additional 30 min and then poured into 100 mL of ice-water. The resulting solution was neutralized with 6M HCl, extracted with

$CHCl_3$, dried (Na_2SO_4), and concentrated. A GLC analysis of the crude product showed a 3:1 starting material to product ratio. The allyl protection procedure was repeated on the isolated crude product using the same amount of NaH and DMF as the solvent; the reaction time was extended to 48 hr. The title compound, 0.58 g (53%) of a yellow oil, was isolated by column chromatography (eluent: 2.5% methanol/dichloromethane): MS z/e (rel. int.) 366 (0.1, M^+), 235 (100), 191 (16).

1-(3'-Methoxy-4'-hydroxyphenyl)-2-propoxyethan-1-ol (42)

Sodium propoxide was prepared under anhydrous conditions by dissolving 11.5 g of freshly cut sodium metal in 500 mL of anhydrous propanol. The excess propanol was removed under high vacuum; the residual sodium salt was dried over calcium sulfate under reduced pressure for 12 hr.

The sodium propoxide and bromoketone **52** were coupled in the manner described for model **36**.[163] The crude product, α-propoxy-3-methoxy-4-hydroxyacetophenone, was isolated as a red oil (15.7 g, 56%) by column chromatography (eluent: 25% ethyl acetate/toluene).

The α-carbonyl group of the acetophenone intermediate was reduced with sodium borohydride according to standard methods.[163] White crystals, 10.2 g (64%), were obtained after recrystallization from ethanol: mp 97-99 °C; IR (cm^{-1}) no carbonyl signals were observed; ^{1}H-NMR ($CDCl_3$) δ 0.94 (t, 3, J = 7.0 Hz, CH_3), 1.63 (sextet, 2, J = 7.2 Hz, $\underline{CH_2}CH_3$), 2.90 (d, 1, J = 2.2 Hz, ROH, exchangeable in D_2O), 3.49

(m, 4, CH_2OCH_2), 3.88 (s, 3, OCH_3), 4.80 (d of d of d, 1, J = 8.8, 3.7, and 2.2 Hz, ArCH), 5.68 (s, 1, ArOH, exchangeable in D_2O), 6.84 (m, 2, $C_{2',5'}$-H), 6.94 (m, 1, $C_{6'}$-H); ^{13}C-NMR ($CDCl_3$) ppm 10.6 (q, CH_3), 22.9 (t, $\underline{CH_2}CH_3$), 55.9 (q, OCH_3), 72.5 (d, ArCH), 73.0 (t, $O\underline{CH_2}C_2H_5$), 76.4 (t, β-CH_2), 108.8 (d, $C_{2'}$), 114.1 (d, $C_{5'}$), 119.1 (d, $C_{6'}$), 132.3 (s, $C_{1'}$), 145.1 (s, $C_{4'}$), 146.4 (s, $C_{3'}$); MS z/e (rel. int.) 226 (14, M^+), 153 (100), 125 (20), 93 (35), 65 (11).

α-Bromo-3-methoxy-4-hydroxyacetophenone (52)

The bromoketone was prepared according to the method reported by Dimmel and Shepard.[163] The bromoketone, which was isolated as a purple solid that contained residual dioxane, could be recrystallized (52.6% recovery) in chloroform/pet ether (2:3)[164] to give white crystals: mp 78.5-81.5 °C (lit. 74-75,[164] 78-79[185]).

α,4-Diacetoxy-3-methoxyacetophenone (53)

The title compound was prepared using the method of Ferrari and Casagrande.[165] In a typical procedure, 72.4 mmols (21.5 g) of crude bromoketone (**52**), which contained residual dioxane, were stirred in 73 mL of freshly distilled acetic anhydride containing 113 mmols (11.09 g) of dry potassium acetate. The mixture was gently refluxed for 15 min and then poured over 500 mL of ice-water. The resulting layers were separated and the aqueous layer extracted twice with 50 mL of $CHCl_3$. The combined organic layers were washed with 2x100 mL of water, dried (Na_2SO_4), and concentrated. The residue was then dissolved in 150 mL of boiling

abs. ethanol and filtered through carbon. Yellowish crystals (12.1 g, 63%) were obtained from the filtrate: mp. 77.5-78.5 °C (lit.[165] 77-78); IR (cm^{-1}) 1760 (ArOAc), 1725 (ROAc), 1675 (RCOAr); ^{1}H-NMR ($CDCl_3$) δ 2.22 (s, 3, ROAc), 2.32 (s, 3, ArOAc), 3.88 (s,3, OCH_3), 5.29 (s, 2, CH_2), 7.12 (d, 1, J = 8.1 Hz, C_5-H), 7.42-7.56 (m, 2, $C_{2,6}$-H); MS z/e (rel. int.) 266 (3, M^+), 224 (29), 151 (100), 123 (10), 43 (25).

α,4-Dihydroxy-3-methoxyacetophenone (54)

Diacetate **53** (10.0 g, 37.6 mmol) was suspended in 150 mL of anhydrous methanol, containing a 1.2 molar excess (45.5 mL) of 0.99M sodium methoxide in methanol. After 25 min at room temperature, the reaction mixture, which had turned dark and contained a white solid, was neutralized with 1M HCl and taken to dryness under reduced pressure. The residue was slurried with decolorizing carbon in warm methanol, filtered, and reduced in volume. The product, 5.31 g (78%) of yellowish crystals, was isolated after recrystallization from methanol: mp 160-162.5 °C (lit.[165] 159-160); IR (cm^{-1}) 3450-3050 (OH), 1675 (RCOAr); ^{1}H-NMR (d_6-DMSO) δ 3.83 (s, 3, OCH_3), 4.71 (s, 2, CH_2), 6.88 (d of d, 1, J = 7.1 and 1.7 Hz, C_5-H), 7.43 (s, 1, C_2-H), 7.48 (d of d, 1, J = 7.6 and 2.0 Hz, C_6-H), the hydroxyl protons were not readily apparent; MS z/e (rel. int.) 182 (11, M^+), 151 (100), 123 (21), 108 (11).

1-(3'-Methoxy-4'-hydroxyphenyl)-1,2-ethanediol (55)

The glycol was prepared by a sodium borohydride reduction from the dihydroxide (**54**) according to the general method of Nonni.[166] The dihydroxide

(5.00 g, 27.4 mmol) was initially dissolved in 500 mL of abs. ethanol. A 10 molar excess of sodium borohydride (10.4 g, 274 mmol) was then added to the stirring solution over a 90 min period. The solution was stirred for an additional 12 hr during which time it was protected from atmospheric moisture by a calcium chloride drying tube. The reaction was quenched with the dropwise addition of glacial acetic acid until effervescing stopped. Upon standing, the mixture thickened and a white solid became evident. The mixture was filtered through a fine glass sintered funnel; the retained white residue was washed with 2x150 mL of abs. ethanol. The filtrate and washes were reduced in volume yielding a yellowish solid. The isolated solid was dissolved in a minimal amount of methanol and prepurified on a short, large diameter, silica gel 60 column with CH_2Cl_2 (500 mL) followed by 25% methanol/dichloromethane as eluents. An oily solid was obtained from the column. The crude product was slurried in 100 mL of hot ethyl acetate and filtered through a fine porosity fritted funnel. The resulting filtrate was reduced in volume yielding an orange oil which was purified by column chromatography (eluent: 5% methanol/dichloromethane). A final yield of 3.66 g (72%) of a light yellow oil was obtained: IR (cm^{-1}) 3600-3000 (OH), no carbonyl signals were observed; ^{1}H-NMR of acetylated* glycol **57**, ($CDCl_3$) δ 2.06, 2.11 (2 s, 6, ROAc), 2.30 (s, 3, ArOAc), 3.83 (s, 3, OCH_3), 4.24-4.36 (d of d of d, 2, J = 11.9, 8.1, and 3.8 Hz, CH_2), 6.01 (d of d, 1, J = 8.1 and 3.8 Hz, CH), 6.96 (d, 1, J = 8.5 Hz, $C_{6'}$-H), 6.97 (s, 1, $C_{2'}$-H), 7.03 (d, 1, J = 8.5 Hz, $C_{5'}$-H);

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* The standard acetic anhydride/pyridine acetylation procedure is described in the section entitled "LOADING CHARACTERIZATION OF THE SUPPORTED MODELS".

the mass spectrum was obtained as a silated (BSA) derivative (58) and was consistent with the data reported by Nonni,[166] MS z/e (rel. int.) 400 (1, M^+), 385 (2), 297 (100), 147 (6), 73 (25).

2-Ethoxy-2-(3'-methoxy-4'-hydroxyphenyl)ethan-1-ol (56)

In oven-dried glassware and under a nitrogen atmosphere, glycol **55** (4.09 g, 22.2 mmol) was dissolved in 200 mL of abs. ethanol following which 5 eq. (111 mL) of anhydrous 1.0M hydrogen chloride in ethanol (Alfa Products) was added. The solution was shaken under a blanket of nitrogen for 24 hr. The acidic solution was neutralized with 4M aq. sodium carbonate. The resulting mixture was filtered through a fine porosity funnel; the retained residue was rinsed with 2x100 mL of abs. ethanol. The combined filtrate was diluted with 100 mL of water and extracted with CH_2Cl_2 (3x50 mL). The organic extract was washed with water (1x100 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure giving a yellow oil. A yield of 2.74 g (58%) of a white solid was obtained after recrystallization in toluene: mp 94.0-96.5 °C; IR (cm^{-1}) 1090 (C-O); ^{1}H-NMR ($CDCl_3$) δ 1.21 (t, 3, J = 7.0 Hz, $OCH_2\underline{CH_3}$), 2.31 (s, 1, ROH, exchangeable in D_2O), 3.35-3.69 (m, 4, $O\underline{CH_2}CH_3$, CH_2OH), 3.90 (s, 3, OCH_3), 4.33 (d of d, 1, J = 8.5 and 3.9 Hz, CH), 5.68 (s, 1, ArOH, exchangeable in D_2O), 6.80 (d, 1, J = 8.1 Hz, $C_{5'}$-H), 6.83 (s, 1, $C_{2'}$-H), 6.89 (d, 1, J = 7.9 Hz, $C_{6'}$-H); MS z/e (rel. int.) 212 (6, M^+), 181 (100), 153 (49), 151 (17), 125 (33), 93 (52), 65 (16). The following spectrum was obtained from the acetylated ethoxide (**61**): ^{1}H-NMR ($CDCl_3$) δ 1.21 (t, 3, J = 7.0 Hz, $OCH_2\underline{CH_3}$), 2.08 (s, 3, ROAc), 2.31 (s, 3, ArOAc),

3.40-3.52 (m, 2, O$\underline{CH_2}CH_3$), 3.84 (s, 3, OCH_3), 4.12-4.21 (d of d of d, 2, J = 11.0, 7.8, and 4.3 Hz, CH_2OAc), 4.51 (d of d, 1, J = 7.6 and 4.2 Hz, CH), 6.91 (d, 1, J = 8.0 Hz, $C_{5'}$-H), 6.97 (s, 1, $C_{2'}$-H), 7.01 (d, 1, J = 8.0 Hz, $C_{6'}$-H). The large shift of the protons on the β-carbon from 3.5 to 4.2 ppm upon acetylation shows that this site was not etherified by treatment with acidic ethanol. The MS, z/e (rel. int.), of the minor products (**59**, **60**) from the etherification are as follows: **1,2-diethoxy-2-(3'-methoxy-4'-hydroxyphenyl)ethane (59)**, 240 (5, M^+), 212 (2), 195 (18), 181 (42), 167 (13), 153 (16), 137 (62), 122 (17), 103 (100), 94 (14), 93 (19), 75 (69), 47 (45); and **2,5-(3'-methoxy-4'-hydroxypheny)-1,4-dioxane (60)**, 332 (25, M^+), 150 (100), 135 (17).

2-Ethoxy-2-(3'-methoxy-4'-allyloxyphenyl)ethan-1-ol (47)

Sodium hydride (34.6 mg, 14.0 mmol) was initially slurried under anhydrous conditions in 20 mL of benzene and 20 mL of DMF. The ethoxide (**56**) (2.98 g, 14.0 mmol) was dissolved in 150 mL of a benzene/DMF (1:2) solution and added dropwise to the stirring NaH mixture. After 30 min, distilled allyl bromide (2.42 mL, 28.0 mmol) dissolved in 50 mL of benzene, was added over a period of 30 min to the reaction mixture which had turned blue. Stirring continued for 24 hr during which time the solution changed to a yellow color. The reaction was quenched by the addition of 30 mL of 1M methanolic sodium methoxide. The resulting solution was stirred an additional 30 min and then diluted with 100 mL of water. The aqueous and organic layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3x50 mL); the extract was added to the initial organic layer. The combined organic

layers were washed with 100 mL of water, dried over Na_2SO_4, and concentrated under reduced pressure. Residual DMF was finally removed from the crude product under high vacuum yielding a yellow oil. The crude material was purified by column chromatography (eluent: 1% methanol/dichloromethane) resulting in 3.09 g (88%) of a light yellow oil: IR (cm^{-1}) 995, 925 ($C=CH_2$); ^{1}H-NMR ($CDCl_3$) δ 1.21 (t, 3, J = 7.0 Hz, $OCH_2\underline{CH_3}$), 2.40 (s, 1, ROH, exchangeable in D_2O), 3.36-3.69 (m, 4, $O\underline{CH_2}CH_3$, CH_2OH), 3.88 (s, 3, OCH_3), 4.35 (d of d, 1, J = 8.5 and 4.0 Hz, ArCH), 4.60 (d of t, 2, J = 5.4 and 1.4 Hz, $ArOCH_2$), 5.35 (d of d of q, J = 17.3, 10.5, and 1.4 Hz, $=CH_2$), 6.03-6.13 (d of d of t, 1, J = 17.3, 10.5, and 1.4 Hz, CH=), 6.80-6.87 (m, 3, Ar-H); ^{13}C-NMR ($CDCl_3$) ppm 15.3 (q, $OCH_2\underline{CH_3}$), 55.9 (q, OCH_3), 64.3 (t, $O\underline{CH_2}CH_3$), 67.2 (t, CH_2OH), 69.9 (t, $ArOCH_2$), 82.4 (d, ArCH), 109.8 (d, $C_{2'}$), 113.1 (d, $C_{5'}$), 118.0 (t, $=CH_2$), 119.2 (d, $C_{6'}$), 131.8 (s, $C_{1'}$), 133.3 (d, CH=), 147.7 (s, $C_{4'}$), 149.1 (s, $C_{3'}$); MS z/e (rel. int.) 252 (13, M^+), 221 (100), 193 (16), 151 (28), 123 (14), 105 (10), 93 (10).

Anal. calcd. for $C_{14}H_{20}O_4$ (%): C, 66.64; H, 7.99; O, 25.37. Found: C, 66.38; O, 7.96; O, 25.66.

Polymer-supported 2-Ethoxy-2-(3'-methoxy-4'-hydroxyphenyl)ethan-1-ol (49)

Sodium hydride (0.263 g, 10.6 mmol) was stirred (overhead) under anhydrous conditions in 25 mL of THF. The allyl-protected lignin model (**47**), dissolved in 75 mL of THF, was added dropwise; stirring continued for 1 hr after the addition was complete. Iodomethylated polystyrene resin **3** (4.51 g, 11.0 mmol) was then added to the stirring solution. After 117 hr, the reaction was stopped. The resin was isolated

by filtration, washed with 4x200 mL of THF, and extracted in a Soxhlet apparatus with THF followed by hexane for 12 and 13 hr, respectively. The resin was finally dried under reduced pressure at 40 °C. A yield of 5.40 g of a light yellow resin was obtained. An analysis of the reaction liquor showed only lignin model **47** to be present indicating that the model was stable under the imposed coupling conditions. The following FTIR signals, either new or enhanced (*) relative to iodomethylated resin **3**, were attributed to the presence of the supported lignin model: 2970 (aliphatic C-H stretch), 1512* (Ar C=C), 1263 and 1224 (Ar-O-R), 1160, 1134, 1103,* 1021* (R-O-R), 996 and 929 (C=C-H), 843 and 810 cm^{-1} (Ar-H). The elemental analysis (in duplicate) was as follows: C, 72.26; H, 6.98; O, 11.29; I, 9.32.

The residual benzyl iodide groups on the heterogeneous intermediate were inactivated by converting them to benzyl methyl ethers. Resin **48** was slurried under anhydrous conditions for 30 min in THF. An excess of sodium methoxide in methanol (140 mL of a 1.1M solution) was added to the mixture. After 72 hr, the reaction was stopped and the resin isolated by filtration. The white resin was washed with 6x100 mL of methanol, acetone, and THF, extracted in a Soxhlet apparatus with hexane for 8 hr, and dried in vacuo at 40 °C. The FTIR showed no significant change from its precursor. The resin was also characterized by high resolution ^{13}C-NMR as previously detailed: ($CDCl_3$) ppm 15.6 ($OCH_2\underline{C}H_3$), 40.4 (polystyrene CH), 40-47 (polystyrene CH_2), 56.3 (OCH_3), 64.6 ($O\underline{C}H_2CH_3$), 69.8 ($ArOCH_2$, $ArCH_2$, β-CH_2), 80 (ArCH), 113 (broad, $C_{2',5'}$), 117.9 (=CH_2), 128.3 (polystyrene omp Ar, $C_{1'}$), 133.5 (CH=), 149 (broad, polystyrene ipso, $C_{3',4'}$), the signal for $ArCH_2O\underline{C}H_3$ is presumably at 56

ppm. The elemental analysis showed a significant loss in the amount of residual iodine: C, 77.74; H, 7.63; O, 12.38; I, 1.94.

The final step in the heterogeneous QM preparation involved removal of the allyl protecting group. Etherified resin **48** was suspended in a warm solution of TTPPR (0.925 g, 1.0 mmol) and Dabco (0.449 g, 4.0 mmol) in 250 mL of an ethanol/ benzene/water (7:3:1 v/v) solvent mixture. The stirring reaction mixture was gently refluxed for 9.5 hr after which it was cooled. The resin, which had turned gray, was isolated by filtration, washed with 5x100 mL of $CHCl_3$, THF, and hexane, and dried at 40 °C under reduced pressure. Once dry, the isomerized resin was slurried in 55 mL of an acetone-water mixture (10:1) containing 1.69 g (6.22 mmol) of yellow $HgCl_2$. The suspension was shaken for 2 hr. The resin was isolated by filtration, washed with 5x100 mL of water, acetone, and ether, and dried at 40 °C under vacuum. The isomerization and mercuric chloride cleavage steps were repeated a second time. After the second $HgCl_2$ treatment, the resin was extracted for 12 hr with hexane and dried. No cleaved model was detected in the liquors from the reaction solutions. The FTIR, relative to intermediate **48**, displayed a strong broad hydroxyl signal at 3600-3100 cm^{-1} and virtually no trace of the allyl signals at 996 and 929 cm^{-1}. Minor changes were observed in the C-O stretch region (approx. 1224 to 1134 cm^{-1}). The FTIR spectrum thus shows that the protecting group was successfully removed with concurrent generation of the desired polymer-bound phenol (**49**). The high resolution ^{13}C-NMR of **49** showed greatly reduced signals at 70, 118, and 134 ppm which

confirms that the allyl group was effectively removed. No iodine or phosphorous were detected in the elemental analysis: C, 75,28; H, 7.11; O, 12.08.

1-Methoxy-1-(3'-methoxy-4'-acetoxyphenyl)ethane (68)

Under anhydrous conditions, 50 mg (0.24 mmol) of the α-ethoxide (**56**) were dissolved in 10 mL of acetonitrile. Iodotrimethylsilane (0.47 mL, 3.30 mmol) was then added to the ethoxide solution via syringe. The resulting mixture was shaken occasionally over a 30 min period. The reaction was quenched by the addition of 6 mL of anhydrous methanol following which pyridine (2.50 mL) was added to neutralize the residual hydroiodic acid. The reaction mixture was concentrated under reduced pressure at 40 °C. The residue was washed with 2x5 mL of anhydrous methanol which was subsequently removed in vacuo. The residue was acetylated by treatment with 7 mL of acetic anhydride, 5 mL of pyridine, and 300 mg of anhydrous sodium acetate. The acetylation was quenched after 24 hr by the addition of cold water (50 mL). The aqueous solution was extracted with 3x10 mL of CH_2Cl_2. The organic extract was washed with 15 mL of 1M HCl followed by 3x15 mL of water. The extract was dried (Na_2SO_4) and concentrated under reduced pressure yielding 68 mg (98%) of a yellow oil: ^{1}H-NMR ($CDCl_3$) δ 1.43 (d, 3, J = 6.5 Hz, CHC$\underline{H}_3$), 2.31 (s, 3, ArOAc), 3.24 (s, 3, CHOC$\underline{H}_3$), 3.84 (s, 3, ArOCH_3), 4.28 (q, 1, J = 6.5 Hz, ArCH), 6.85 (d of d, 1, J = 8.1 and 1.8 Hz, $C_{5'}$-H), 6.95 (d, 1, J = 1.7 Hz, $C_{2'}$-H), 6.99 (d, 1, J = 8.0 Hz, $C_{6'}$-H); ^{13}C-NMR ($CDCl_3$) ppm 20.7 (q, CH_3C=O), 24.0 (q, CHC$\underline{H}_3$), 55.9 (ArOCH_3), 56.6 (q, CHOC$\underline{H}_3$), 79.4 (d, ArCH), 109.8 (d, $C_{2'}$), 118.5 (d, $C_{6'}$), 122.5 (d, $C_{5'}$), 138.9 (s, $C_{1'}$), 142.5

(s, $C_{4'}$), 151.2 (s, $C_{3'}$), 169.1 (s, C=O); MS z/e (rel. int.) 224 (4, M^+), 182 (17), 167 (100), 153 (32), 152 (15), 151 (33), 135 (10), 121 (12), 119 (12), 91 (23), 79 (14), 77 (17), 43 (29).

The MS, z/e (rel. int.), for aldehyde **62**, which was obtained as a significant side product (48%) when the isomerized starting material (**47**) was treated with dilute HCl in acetone, is as follows: 166 (31, M^+), 137 (100), 122 (19), 94 (10).

1-Ethoxy-1-(3'-methoxy-4'-hydroxyphenyl)-2-benzyloxyethane (80)

Under anhydrous conditions, 171 mg (1.2 eq.) of NaH were slurried in DMF at 45 °C. After 10 min, allyl-protected compound **47** (1.45 g, 5.75 mmol, 1 eq.), dissolved in 50 mL of DMF, was dripped into theNaH slurry. Benzyl bromide (2.73 mL, 4 eq.) in 20 mL of DMF was then slowly added to the reaction mixture which had been stirring for 60 min. Stirring was maintained at 45 °C for a total of 154 hr. The reaction was quenched by carefully adding 46 mL (8 eq.) of 1M sodium methoxide in methanol; the resulting solution was stirred for 3 hr while cooling to room temperature. The reaction liquor was diluted with water (200 mL), extracted with $CHCl_3$ (2x100 mL), and dried over Na_2SO_4. The organic extract was concentrated under reduced pressure to evaporate the $CHCl_3$. The residual DMF was removed under high vacuum at 43 °C. Analysis of the product mixture by GLC showed that the starting material had not been completely consumed.

The crude product was benzylated a second time in order to improve the yield. The level of NaH was adjusted to 137 mg; the reaction time was 114 hr at 46

°C. Analysis of the resulting product mixture revealed that a significant level of the residual starting material (**47**) had been consumed, although not completely. The benzylated product was isolated by column chromatography (eluent: 20% ethyl acetate/toluene). A second column of 1% ethyl acetate/dichloromethane followed by 1% ethyl acetate/1% methanol/dichloromethane was required for purification. An intermediate yield of 1.01 g (51%) of a light yellow oil was obtained: ^{1}H-NMR ($CDCl_3$) δ 1.05 (t, 3, J = 6.8 Hz, $OCH_2\underline{CH_3}$), 3.27, 3.28 (2 q, 2, J = 7.0 Hz, $O\underline{CH_2}CH_3$), 3.35 (d of d, 1, J = 10.4 and 4.1 Hz, $CHC\underline{H_A}H_B$), 3.51 (d of d, 1, J = 10.4 and 7.6 Hz, $CHCH_A\underline{H_B}$), 3.69 (s, 3, OCH_3), 4.28 (d of d, 1, J = 7.6 and 4.1 Hz, $\underline{CH}CH_AH_B$), 4.34 (d, 1, J = 12.2 Hz, $OC\underline{H_M}H_NAr$), 4.44 (d of t, 2, J = 5.4 and 1.4 Hz, $ArOCH_2$), 4.48 (d, 1, J = 12.3 Hz, $OCH_M\underline{H_N}Ar$), 5.17 (d of d of q, 2, J = 17.3, 10.5, and 1.4 Hz, $=CH_2$), 5.88-5.96 (d of d of t, 1, J = 17.3, 10.5, and 1.4 Hz, CH=), 6.64-6.70 (m, 3, Ar-H), 7.09-7.17 (m, 5, Ar-H of benzyl); MS z/e (rel. int.) 342 (4, M^+), 221 (100), 193 (21), 165 (11), 137 (14), 133 (11), 124 (12), 105 (16), 91 (56), 77 (10), 65 (11).

The allyl ether protecting group was removed from the intermediate product by first converting it to a prop-1-enol ether with TTPPR/Dabco. Initially, 783 mg (2.29 mmol, 14.6 eq.) of the benzylated intermediate were refluxed for 28 hr in 60 mL of an ethanol/benzene/water (7:3:1) solvent mixture containing 1 eq. (145 mg) of TTPPR and 4 eq. (71 mg) of Dabco. Once the reaction mixture had cooled, it was diluted with water (30 mL) and extracted with CH_2Cl_2 (3x30 mL); the CH_2Cl_2 was then removed under reduced pressure. Next, the resulting prop-1-enol ether was dissolved in 25 mL of an acetone/water (10:1) solvent mixture containing 747 mg

(1.5 eq.) of yellow HgO to which $HgCl_2$ (627 mg, 1 eq.) in 10 mL of the acetone/water solution was added over a period of 5 min. The combined reaction mixture was shaken for 1 hr, filtered through ceilite to remove the HgO, and reduced in volume. The residual material was diluted with 30 mL of CH_2Cl_2, washed with a sat. aq. potassium iodide solution (10 mL), dried (Na_2SO_4), and concentrated under reduced pressure. A white solid (0.50 g, 72%) was obtained after purification by column chromatography (eluent: 20% ethyl acetate/toluene followed by a second column of 1% methanol/dichloromethane): mp 75-77 °C; ^{1}H-NMR ($CDCl_3$) δ 1.15 (t, 3, J = 7.0 Hz, $OCH_2\underline{CH_3}$), 3.42, 3.43 (2 q, 2, J = 7.0 Hz, $O\underline{CH_2}CH_3$), 3.50 (d of d, 1, J = 10.4 and 4.1 Hz, $CHC\underline{H_A}H_B$), 3.66 (d of d, 1, J = 10.4 and 8.6 Hz, $CHCH_A\underline{H_B}$), 3.85 (s, 3, OCH_3), 4.38 (d of d, 1, J = 7.6 and 4.1 Hz, $\underline{CH}CH_AH_B$), 4.45 (d, 1, J = 12.3 Hz, $OC\underline{H_M}H_NAr$), 4.58 (d, 1, J = 12.3 Hz, $OCH_M\underline{H_N}Ar$), 5.55 (s, 1, ArOH, exchangeable in D_2O), 6.73-6.83 (m, 3, Ar-H), 7.20-7.26 (m, 5, Ar-H of benzyl); ^{13}C-NMR ($CDCl_3$) ppm 15.4 (q, $OCH_2\underline{CH_3}$), 55.9 (q, OCH_3), 64.4 (t, $O\underline{CH_2}CH_3$), 73.4, 74.8 (2 t, $CH\underline{CH_2}$ and $ArCH_2$), 81.2 (d, ArCH), 109.0 (d, $C_{2'}$), 114.0 (d, $C_{5'}$), 120.1 (d, $C_{6'}$), 127.5 (d, C_4 of benzyl), 127.7 (d, $C_{3,5}$ of benzyl), 128.3 (d, $C_{2,6}$ of benzyl), 131.9 (s, $C_{1'}$), 138.4 (s, C_1 of benzyl), 145.3 (s, $C_{4'}$), 146.6 (s, $C_{3'}$); MS z/e (rel. int.) 302 (3, M^+), 181 (69), 153 (43), 152 (28), 151 (33), 137 (20), 133 (30), 125 (29), 93 (34), 91 (100), 77 (22), 65 (40).

Anal. calcd. for $C_{18}H_{22}O_4$ (%): C, 71.50; H, 7.33; O, 21.17. Found: C, 69.93; H, 7.11, O, 20.18.

Attempts to prepare the title compound by selectively adding a benzylate anion to bromoketone **52** followed by reduction of the α-carbonyl and subsequent etherification of the resulting α-hydroxide were unsuccessful. Unidentified products were obtained during the initial addition step.

1-(3',5'-Dimethoxy-4'-hydroxyphenyl)-1-(3''-methoxy-4''-hydroxyphenyl)-2-benzyloxyethane (79)

The soluble C1-Cα dimer (**79**) was prepared by cooking 43.9 mg (0.145 mmol) of model **80** with 3 eq. of syringol (**43**) in 0.050M NaOH for 15 min at 170 °C. The preparation of the "minibombs", each containing approximately 0.0200 mmol of **80**, and conduction of the cook, are described later in a section entitled HIGH TEMPERATURE REACTIONS — GENERAL METHOD. The contents of the minibombs, once cool, were emptied into a common container. The alkaline rinses (2x3 mL of 0.050M NaOH) of each bomb were also added to the container. The combined reaction liquors and washes were acidified to pH 5 with 5M acetic acid and extracted with CH_2Cl_2 (4x10 mL). The CH_2Cl_2 was then removed under reduced pressure. The dimer was isolated from the residual material by column chromatography (eluent: 1% methanol/dichloromethane). A final yield of 26.6 mg (45%) of a yellow oil was obtained: ^{1}H-NMR ($CDCl_3$) δ 3.80 (s, 3, OCH_3''), 3.81 (s, 6, OCH_3'), 4.18 (t, 1, J = 7.1 Hz, ArCH), 4.60 (d, 2, J = 3.4 Hz, β-CH_2), 5.30 (s, 2, $ArCH_2$), 5.44, 5.50 (2 s, 2, ArOH, exchangeable in D_2O), 6.44 (s, 2, $C_{2',6'}$-H), 6.70-6.74 (m, 2, $C_{2'',5''}$-H), 6.85 (d, 1, J = 8.1 Hz, $C_{6''}$-H), 7.26-7.39 (m, 5, Ar-H of benzyl); ^{13}C-NMR ($CDCl_3$) ppm 50.7 (d, ArCH), 55.9 (q, OCH_3''), 56.3 (q, OCH_3'), 73.2 (t, $ArCH_2$), 73.8 (t, β-CH_2), 105.2 (d, $C_{2',6'}$), 111.2

(d, $C_{2''}$), 114.1 (d, $C_{5''}$), 120.9 (d, $C_{6''}$), 127.6 (d, C_4 of benzyl), 127.8 ($C_{3,5}$ of benzyl), 128.3 ($C_{2,6}$ of benzyl), ≈ 132.2 ($C_{1'}$), 133.5 (s, $C_{4'}$), 134.2 ($C_{1''}$), 138.2 (s, C_1 of benzyl), 144.1 (s, $C_{4''}$), 146.3 (s, $C_{3''}$), 146.8 (s, $C_{3',5'}$); the dimer was methylated (dimethylsulfate) before MS, z/e (rel. int.), analysis: 438 (12, M^+), 317 (100), 91 (35).

LOADING CHARACTERIZATION OF THE SUPPORTED MODELS

The loading of the trityl ether linked heterogeneous model (**5**) was determined by methoxyl analysis. Quantification by cleavage of the trityl ether linkage with trifluoroacetic acid yielded inconsistent results.[74]

The following two sections detail the gravimetric and iodotrimethylsilane methods for determining the level of model attached to the resin through a benzyl ether linkage (**6** and **49**).

Gravimetric Method

The gravimetric loading value was determined from the weight increase observed when coupling the ligninlike model (**25** or **47**) to the functionalized resin support (**3**). Equation 13, which was adapted from an equation developed by Apfeld[74] for calculating the gravimetric loading of a model bound through a polymer-supported trityl ether linkage, was used to determine the loading when employing iodomethylated polystyrene as a support:

$$[\text{model loading (g)}] = \frac{[\text{weight gain of polymer product}]}{1 - \frac{[\text{MW of HI}]}{[(\text{MW of model}) - 1]}} \quad [13]$$

For example, the amount of material loaded on **27**, 2.44 g, corresponds to a loading value of 1.57 mmol of model per gram of resin. Equation 13 is directly applicable to the heterogeneous QM model (**48**) by changing the MW (molecular weight) value.

Iodotrimethylsilane (ITS) Method

Polymer-supported Phenol System

Under a nitrogen atmosphere, 1.00 mL of dry acetonitrile was added to a dark vial containing 20-25 mg of the dry heterogeneous model (**6**). After the resin had soaked for 15 min, 0.035-0.040 mL (approx. 1.5-2.0 eq. per oxygen atom) of ITS was added to the vial via syringe. The vial was sealed and shaken occasionally over a 30 min period. The reaction was quenched by adding 0.50-0.75 mL of anhydrous methanol containing internal standard (4-ethoxyphenol). The reaction liquor was pipetted from the beads and added to 0.25 mL of pyridine. The resulting solution, along with 3x1 mL methanol rinses of the reacted resin, was concentrated under reduced pressure at a maximum of 40 °C. The residue was then added to 0.50 mL of dry pyridine, 0.75 mL of acetic anhydride, and 30 mg of anhydrous sodium acetate. After shaking for 24 hr, the acetylation mixture was treated with 4x2.5 mL aliquots of cold water and extracted with 2x5 mL of CH_2Cl_2. The organic extract was washed with 5 mL of 1M HCl followed by 3x5 mL of water, then dried (Na_2SO_4), and

concentrated under reduced pressure with no applied heat. The residual material was dissolved in 2 mL of CH_2Cl_2, stored in a dark vial over Na_2SO_4, and analyzed by GLC. The MS, z/e (rel. int.), for the compounds (**29-32**) observed in the ITS product mixture were as follows: **1-acetoxy-3-(3'-methoxy-4'-acetoxyphenyl)propane (29)**, 266 (12, M^+), 224 (83), 164 (100), 149 (40), 137 (79), 133 (25), 132 (22), 131 (15), 122 (10), 107 (10), 91 (15), 77 (11), 43 (28); **1-iodo-3-(3'-methoxy-4'-acetoxyphenyl)propane (30)**, 334 (5, M^+), 292 (62), 155 (10), 137 (100), 43 (8); **1-acetoxy-3-(3',4'-diacetoxyphenyl)propane (31)**, 294 (6, M^+), 252 (29), 210 (94), 150 (100), 149 (19), 133 (10), 132 (19), 131 (9), 123 (29), 122 (16), 91 (10), 77 (14), 43 (93); and **1-acetoxy-3-(3'-methoxy-4'-propoxyphenyl)-propane (32)**, 266 (84, M^+), 206 (6), 179 (7), 164 (94), 163 (19), 149 (34), 137 (100), 133 (28), 132 (18), 131 (18), 91 (20), 77 (18), 43 (57).

A loading value of 1.29 ± 0.04 mmol/g was obtained employing the conditions cited above. Increasing the reaction time to 90 min or the number of ITS equivalents (to approx. 5) lowered the loading values to 1.21 and 1.16 mmol/g, respectively. Raising the reaction temperature to 70 °C had a pronounced adverse effect as the loading level was reduced to 0.15 mmol/g. A loading of 1.35 ± 0.05 mmol/g was obtained by replacing acetonitrile with carbon tetrachloride. Use of carbon tetrachloride was not continued since the suspended beads tended to cling out of solution onto the walls of the vial. It was felt that the reproducibility over multiple samples would not be as high as the initial tests indicated.

The reacted resin was isolated by filtration and washed with 5x2 mL aliquots of the following solvents: methanol, ether, pet. ether, and hexane. The resin was dried in a vacuum oven at 40 °C before being analyzed by FTIR.

A portion (10 mg) of the isolated ITS treated resin was powdered and shaken for 3.5 hr in 2 mL of 1M citric acid monohydrate in methanol.[146] The resin was isolated by filtration and washed with the solvents used in the above isolation procedure. The FTIR spectrum was discussed in the text.

Polymer-supported Quinone Methide System

The ITS procedure as described above was employed with only a slight modification for supported QM model **49**. The change involved increasing the quantity of the ITS reagent to 0.050-0.055 mL to account for the additional benzyl ether bond on the attached monomer. The MS, z/e (rel. int.), for ethanol queched **69** and minor components **70** and **71**, were as follows: **1-ethoxy-1-(3'-methoxy-4'-acetoxyphenyl)ethane (69)**, 238 (6, M^+), 196 (31), 181 (100), 153 (28), 151 (26), 125 (13), 93 (12), 91 (10), 43 (16); **1-ethoxy-1-(3'-methoxy-4'-acetoxyphenyl)ethan-2-ol (70)**, 254 (2, M^+), 223 (2), 181 (6), 149 (3), 137 (6), 75 (100), 43 (3); and **1,4'-diacetoxy-2,3'-dimethoxy-2-phenylethane (71)**, 282 (1, M^+), 240 (3), 209 (6), 180 (4), 167 (100), 152 (7), 151 (7), 43 (11).

Soluble C1-Cα dimer **79** (13 mg, 0.032 mmol) was treated with an excess of ITS (0.040 mL, 0.14 mmol) for 25 min at room temperature. The reaction was quenched with anhydrous methanol and the resulting product acetylated. Observation of the

debenzylated material, **1-(3',5'-dimethoxyphenyl)-1-(3"-methoxyphenyl)-2,4',4"-triacetoxyethane**, showed that the C1-Cα dimer was stable under the imposed ITS conditions and thus should be stable if formed on the resin: MS z/e (rel. int.) 446 (2, M^+), 344 (40), 302 (100), 289 (44), 43 (13).

HIGH TEMPERATURE REACTIONS — GENERAL METHOD

The simulated pulping reactions were performed under nitrogen in small (4 mL capacity) stainless steel pressure vessels (bombs). Once the bombs were placed in the constant temperature oil bath, a three minute warm-up time was allowed before recording time zero. Likewise, a three minute cool-down period was given between the time the bombs were removed from the oil bath and quenched with ice-water. The bombs were slowly rotated end-over-end to facilitate mixing. All pulping-type reactions were conducted in 1.00M NaOH; the standard volume of solution per bomb was 3.5 mL. The 1.00M NaOH stock was freshly prepared before each trial from concd. ultrapure sodium hydroxide (Alfa Products) and oxygen-free distilled water. The kinetic experiments were performed in duplicate unless otherwise noted; GLC analyses were also done in duplicate for each sample. The internal standard for all reactions at 170 °C was 4-ethoxyphenol in 1.00M NaOH.

HYDROLYSIS OF POLYMER-SUPPORTED BENZYL IODIDE

The bombs were loaded with 100 mg (0.31 mmol) of polymer-bound benzyl iodide and 1.00M NaOH. Cooks were carried out according to the standard high

temperature method at 130, 150 and 171 °C. The cooled, reacted resin was filtered and washed with 3x5 mL of water, methanol, and acetone. The beads were finally extracted in a Soxhlet apparatus for 4 hr with hexane and dried at 50 °C in a vacuum oven.

The pseudo first order kinetic equation took the following form: $\ln R = k't + \ln R_0$. The rate constant, k', was determined by plotting reaction time (sec) vs. the ln R, where R is the benzyl iodide loading. The activation energy (E) was calculated from the Arrhenius equation: $k' = Ae(-E/RT)$.

STABILITY OF THE POLYMER-MODEL LINKAGES

Trityl Ether Stability

Polymer-supported guaiacylpropanol (**5**) was cooked at 147 °C in 1.00M NaOH for varying periods between 1 and 4 hr following the general procedure outlined in the HIGH TEMPERATURE REACTIONS section. Each bomb contained 200 mg (0.44 mmol) of heterogeneous model.

Once the bombs were cool, the contents were filtered and washed with 3x5 mL of the following solvents: water, water/methanol (1:2), methanol, CH_2Cl_2, and low boiling pet. ether. The resin was then extracted in a Soxhlet apparatus with ether and hexane for 8 hr each, and finally dried under reduced pressure at 45 °C. The quantity of model remaining on the resin was determined by methoxyl analysis.

Benzyl Ether Stability

Each bomb contained 25 mg of the heterogeneous model (**6**). Two separate trials at 169 and 171 °C were performed. Internal standard was added volumetrically to the cooled bombs following which the liquor was pipetted off the resin and added to a 50 mL flask. Alkaline rinses (1M NaOH, 3x2 mL) of the remaining resin were also added to the flask. The combined reaction liquor was then acidified with 2.50 mL of 5M acetic acid. Water was removed from the sample under reduced pressure at a maximum temperature of 40 °C. The residue was further dried by adding 5 mL of isopropyl alcohol which was then removed in vacuo. The product was acetylated with 0.75 mL of dry pyridine and 2.25 mL of acetic anhydride and isolated as previously described. The reaction mixture was quantitatively analyzed by GLC for guaiacylpropanol (**15**).

After the 4-ethoxyphenol had been added and mixed with the reaction liquor as described above, a 1 mL aliquot was removed from selected samples and analyzed for ethanol.[186] Each aliquot was added to 0.25 mL of 2M sulfuric acid after which methanol was added as an internal standard. The samples were analyzed on a 6 ft. x 2 mm ID Super Q column (program: isothermal at 135 °C; inj. temp. 200 °C; FID detect. temp. 300 °C; helium carrier gas (20 mL/min)).

The beads were isolated by filtration, rinsed initially with 1M NaOH as described above, and then washed successively with 5x2 mL of water, 50% aq. dioxane, 50% 1M acetic acid/dioxane, water, abs. ethanol, and anhydrous ether. The isolated

resin was finally dried in a vacuum oven at 40 °C. The level of model remaining on the resin was determined by the ITS method.

The heterogeneous model (**3**) was conditioned (75 mg resin per bomb) in 1.00M NaOH at 169 °C for 90 min. Once cool, the reaction mixture was filtered and the collected resin washed with 5x100 mL of the above solvents and dried for several days in vacuo at 40 °C. The beads were characterized by FTIR and the ITS method. The ITS product solution from the conditioned resin revealed, in addition to the previously identified compounds (**29 - 32**), the presence of **1-(3'-methoxy-5'-allyl-phenyl)-3,4'-diacetoxypropane (33)**: MS z/e (rel. int.) 306 (10, M^+), 264 (100), 210 (13), 204 (24), 177 (53), 163 (19), 150 (16), 137 (11), 131 (10), 115 (10), 91 (13), 44 (13), 43 (56), 40 (29).

CONDENSATION REACTIONS

Polymer-supported Phenol System

The bombs were prepared in the usual manner. The concentration of syringyl alcohol (**72**) was 0.0200 mmol per bomb for both the homo- and heterogeneous reactions; the concentration of guaiacylpropane (**4** or **6**) was 0.0250 mmol per bomb. The guaiacylpropane loading in the heterogeneous system was based on the ITS loading value of 0.81 mmol/g (30.9 mg resin per bomb). The homogeneous system contained inert polymer-bound benzyl ethoxide (32.0 mg/bomb) to eliminate any resin induced effects. In the heterogeneous case, an additional (single) cook was

performed to confirm the results obtained from the initial (duplicate) experiment. The temperature of the homogeneous trial was 172 °C, the heterogeneous reactions were conducted at 170 °C.

The bombs were cooled in ice-water, opened, and internal standard added volumetrically. The resin was isolated by filtration. The bombs and isolated resin were washed with 3x3 mL of 1M NaOH. The reaction liquor and washes were then combined and methylated. The methylation procedure consisted of adding 1 mL of dimethylsulfate to each solution and stirring for 40 min. The methylation was quenched by adding 4 mL (excess) of 40% aqueous dimethylamine and stirring for 15 min. Dichloromethane (4 mL) was then added and stirring continued for an additional 5 min. The contents of the reaction flask were added to a separatory funnel along with 3x4 mL water rinses. The layers were separated and the aqueous layer extracted twice more with 4 mL of CH_2Cl_2. The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure at room temperature. The solutions were quantitatively analyzed by GLC. The MS, m/e (rel. int.), of the methylated reaction products were as follows: **3',4'-dimethoxyphenylpropane**, 180 (30, M^+), 151 (100), 107 (7), 91 (5), 77 (6); **3,4,5-trimethoxybenzyl alcohol**, 198 (100, M^+), 183 (21), 181 (10), 155 (10), 127 (34), 123 (13), 95 (19); **3,4,5-trimethoxybenzene**, 168 (100, M^+), 153 (79), 125 (48), 110 (74), 108 (13), 107 (14), 95 (56), 93 (36), 77 (20), 65 (23), 53 (14), 51 (23), 50 (11), 39 (41); **3,4,5-trimethoxytoluene**, 182 (94, M^+), 167 (100), 139 (53), 124 (49), 109 (43), 107 (36), 91 (11), 79 (19), 77 (15), 65 (13), 53 (30); **3,4,5-trimethoxybenzaldehyde**, 196 (100, M^+), 195 (6), 181 (49), 125 (33), 110 (30), 95 (21), 93 (15), 77 (11), 65 (11), 51 (11), 39

(17); **3,3',4,4',5,5'-hexamethoxydiphenylmethane**, 348 (100, M^+), 333 (11), 302 (11), 301 (13), 287 (6), 271 (6), 258 (12), 243 (7), 181 (8), 143 (8); **2,3,3',4',5'-pentamethoxy-5-propyldiphenylmethane**, 360 (100, M^+), 345 (14), 331 (10), 329 (11), 270 (13), 181 (33), 151 (11).

Functionalization of the benzylic hydroxyl group of syringyl alcohol was incomplete as two derivatives, 3,4,5-trimethoxybenzyl alcohol and 3,4,5-trimethoxybenzylmethyl ether, were consistently observed. The reported amounts of syringyl alcohol were therefore composites of the quantities of the two moieties detected. A GLC response factor for 3,4,5-trimethoxybenzyl alcohol was determined directly on a purchased sample (Aldrich); 3,4,5-trimethoxybenzylmethyl ether was prepared from the benzyl alcohol for response factor calibrations.

The resin from the heterogeneous reaction was isolated by filtration and washed as described for the stability test. The beads were then dried in vacuo at 40 °C before ITS analysis. A response factor for the GLC analysis of ITS cleaved C5-Cα dimer (acetylated **77**) was estimated from homogeneous dimer **8**, which was acetylated according to the conditions described for the ITS method. The MS, z/e (rel. int.), of acetylated heterogeneous C5-Cα dimer (**77**), **2,3'',4'-triacetoxy-3,3',5'-trimethoxy-5-propyldiphenylmethane**, was as follows: 474 (3, M^+), 432 (51), 390 (100), 237 (12), 176 (15), 167 (27), 154 (50), 43 (23).

The average mass balance for the heterogeneous reaction was 83.4 ± 4.0%, based on syringyl alcohol; based on polymer-bound guaiacylpropanol, the average

mass balance was 93.2 ± 8.8%. Mass balance data for the solution phase reaction could not be obtained due to incomplete GLC resolution of guaiacylpropane (**4**) and 4-methylsyringol (**75**). The FTIR spectrum of the polymer-bound benzyl ethoxide after the homogeneous trial was similar to that of the unreacted material.

A control cook of syringyl alcohol (**72**) alone (0.0200 mmol/bomb), at 170 °C in 1.00M NaOH, was conducted in the usual manner. As in the guaiacylpropane-syringyl alcohol reaction, inert polymer-supported benzyl ethoxide was added (32.0 mg/bomb) to eliminate any resin effects.

Preliminary solution phase condensation reactions were conducted at 150 °C in 1.00M NaOH for up to 4 hr. The reactions examined were (a) the self condensation of syringyl alcohol (0.0200 mmol/bomb) and (b) guaiacylpropane-syringyl alcohol condensation (0.0200 mmol/bomb each). No inert resin substrate was added in either reaction. The internal standard, 4-methylanisole, was added after the reaction mixture had been methylated.

Polymer-supported Quinone Methide System

All condensation reactions and product isolations involving soluble and insoluble QM models **80** and **49** were conducted according to standard methods. A quantity of 0.0200 mmol of QM model per bomb (24.1 mg of **49** per bomb) was employed in all cases; specific conditions were described in the text. The MS, z/e (rel. int.), for hydrolyzed/methylated starting material **80** and (methylated) vinyl ether **81**

were as follows: **1-phenyl-2-benzyloxy-1,3',4'-trimethoxyethane (80)**, 302 (0.2, M^+), 181 (13), 165 (100), 137 (8), 122 (5), 107 (5), 91 (10), 77 (10), 65 (5); and **1-(3',4'-dimethoxyphenyl)-2-benzyloxyethene (81)**, 270 (18, M^+), 241 (12), 179 (100), 165 (23), 151 (65), 148 (29), 136 (13), 121 (13), 107 (14), 91 (81), 77 (15), 65 (24). The MS of the Claisen rearranged product, **4'-acetoxy-5'-allyl-1,3'-dimethoxyphenylethane**, detected in the ITS product mixture of reacted **49**,was as follows: 264 (4, M^+), 222 (33), 207 (100), 191 (16), 91 (10), 43 (20).

The acetolysis procedure employed on a sample of reacted ITS treated resin was described by Bovee.[75] The acetolysis reagent ratio was, however, modified to the following: glacial acetic acid : acetic anhydride : concd. sulfuric acid (1:1:0.4). Benzyl ether cleavage of model **80** via acetolysis was nearly quantitative and led to **3'-methoxyphenyl-1,2,4'-triacetoxyethane**: MS z/e (rel. int.) 310 (2, M^+), 208 (34), 166 (83), 153 (100), 137 (8), 93 (14), 43 (98).

The condensation reaction between the soluble propoxy model (**42**) and syringol (**43**) was carried out at 150 °C in 0.050M NaOH for 1 hr according to standard methods. The following are the MS, z/e (rel. int.), of the corresponding (methylated) C1-Cα dimer (**44**) and cis/trans vinyl ether (**45**) products: **1-(3',4',5'-trimethoxyphenyl)-1-(3",4"-dimethoxyphenyl)-2-propoxyethane (44)**, 390 (10, M^+), 318 (19), 317 (100), 43 (9); and **1-(3',4'-dimethoxyphenyl)-2-propoxyethene (45)**, 222 (100, M^+), 180 (50), 179 (32), 165 (37), 151 (47), 148 (15), 91 (13), and 222 (100, M^+), 180 (59), 179 (36), 165 (45), 151 (56), 148 (18), 91 (13).

RECOMMENDATIONS

The results of this study have shown that polymer-supported models can be used effectively to study pulping reactions in a controlled, two-phase environment. As was also demonstrated, not all aspects of the heterogeneous models are straightforward. More fundamental work directed at improving synthetic procedures, model design, and characterization will be required before supported models become fully functional as a research tool. Several other applications, in pursuit of these objectives, are conceivable. Determining the effectiveness of pulping additives (HS^-, $AHQ^=$) at inhibiting condensation on soluble vs. insoluble quinone methides is one example. In this regard, heterogeneous models represent a resource which remains largely unexplored.

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LITERATURE CITED

1. Fengel, D.; Wegener, G. Wood, Chemistry, Ultrastructure, Reactions. New York, Walter de Gruyter, 1984:Chapters 3, 4, 6, and 11.

2. Clerman, L.; Schwartz, H., Pulp Paper Mag. Can. 52:103(1951).

3. Adler, E., Wood Sci. Technol. 11:169(1977).

4. Freudenberg, K. In Constitution and Biosynthesis of Lignin. K. Freudenberg and A. Neish (Eds.), New York, Springer-Verlag, 1988:47-122.

5. Glasser, W.; Glasser, H., Pap. Puu 63:71(1981).

6. Gierer, J., Wood Sci. Technol. 14:241(1980).

7. Ljunggren, S., Svensk Papperstidn. 83:363(1980).

8. Axegård, P.; Wikén, J.-E., Sven. Papperstidn. 86:R178(1978).

9. Sjöblom, K.; Mjöberg, J.; Hartler, N., Pap. Puu 65:227(1983).

10. Singh, R. In The Bleaching of Pulp. R. Singh (Ed.), 3rd ed., Atlanta, TAPPI PRESS, 1979:15-22.

11. Bryce, J. In Pulp and Paper, Chemistry and Chemical Technology. J. Casey (Ed.), Vol. 1, 3rd ed., New York, J. Wiley and Sons, Inc., 1980:428-429. Also W. Glasser, ibid, p. 69-76.

12. Marton, J. In Lignins, Occurrence, Formation, Structure, and Reactions. K. Sarkanen and C. Ludwig (Eds.), New York, J. Wiley and Sons, Inc., 1971:Ch. 16.

13. Gierer, J.; Imsgard, F.; Pettersson, I., Appl. Polym. Symp. 28:1195(1976).

14. Gierer, J., Wood Sci. Technol. 19:289(1985).

15. Brunow, G.; Miksche, G., Appl. Polym. Symp. 28:1155(1976).

16. Miksche, G., In Chemistry of Delignification With Oxygen, Ozone, and Peroxides. Tokyo, UNI Publishers Co., Ltd., 1980:107.

17. Gierer, J.; Ljunggren, S., Svensk Papperstidn. 82:503(1979).

18. Smith, D. The Demonstration of Electron-Transfer Reactions and Their Effect on Model Lignin Condensation Reactions Under Alkaline Pulping Conditions. Doctoral Diss., The Institute of Paper Chemistry, Appleton, WI, 1986. 115p.

19. Dimmel, D.; Shepard, D.; Brown, T., J. Wood Chem Technol. 1:123(1981).

20. Gierer, J.; Söderberg, S.; Thoren, S., Svensk Papperstidn. 66:990(1963).

21. Dimmel, D.; Shepard, D., J. Wood Chem. Technol. 2:73(1982).

22. Araki, H.; Hawes, D.; Schroeter, M.; Chen, C-L.; Gratzl, J., Can. Wood Chem. Symp., Harrison Hot Springs, BC, Canada, 1979:71.

23. Fullerton, T., J. Wood Chem. Technol., 7:441(1987).

24. Kratzl, K.; Wagner, I., Holzforschung und Holzverwertung 24:56(1972).

25. Lindeberg, O. Studies on the Chemistry of Delignification in Alkaline Media, Doctoral Diss., University of Stockholm, Sweden, 1979.

26. Johansson, B.; Miksche, G., Acta Chem. Scand. 23:824(1969).

27. Ishizu, A.; Nakano, J.; Oya, H.; and Migita, N., J. Japan Wood Res. Soc. 4:176(1958).

28. Gierer, J.; Pettersson, I., Can. J. Chem. 55:593(1977).

29. Gierer, J.; Lindeberg, O., Acta Chem. Scand. B33:580(1979).

30. Brown, W.; Cowling, E.; Falkehag, S., Svensk Paperstidn. 71:811(1968).

31. Chiang, V.; Stokke, D., J. Wood Chem. Technol. 9:61(1989).

32. Sorvari, J.; Sjöström, E.; Klemola, A.; Laine, J., Wood Sci. Technol., 20:35(1986).

33. Obiaga, T.; Wayman, M., Svensk Papperstidn. 76:699(1973) and Appl. Polym. Symp. 18:1943(1974).

34. Fleming, B.; Kubes, G.; MacLeod, J.; Bolker, H., Tappi 61(6):43(1978).

35. Farrington, A.; Nelson, P.; Vanderhoek, N., Appita 32:300(1979).

36. Brown, T. The Effect of Anthraquinone on the Molecular Weight Distribution of Loblolly Pine Dioxane Lignin During Alkaline Cooks. MS Diss., The Institute of Paper Chemistry, Appleton, WI, 1979. 41p.

37. Kondo, R.; McCarthy, J., J. Wood Chem. Technol. 5:37(1985).

38. Mortimer, R., J. Wood Chem. Technol. 2:383(1982).

39. Kwoh, D.; Bhattacharjee, S.; Cael, J.; Patt, S., TAPPI R&D Conf. Proc., Asheville, NC, 1982:113.

40. Robert, D.; Bardet, M.; Gellerstedt, G.; Lindfors, E., J. Wood Chem. Technol. 4:239(1984).

41. Gellerstedt, G.; Gustafsson, K., J. Wood Chem. Technol. 7:65(1987).

42. Gellerstedt, G.; Gustafsson, K.; Northey, R., Nordic Pulp Paper Res. J. 3:87(1988).

43. Glasser, W.; Barnett, C.; Sano, Y., J. Appl. Polym. Symp. 37:441(1983).

44. Obst, J.; Landucci, L.; Sanyer, N., Tappi 62(1):55(1979).

45. Landucci, L., J. Wood Chem. Technol. 4:171(1984).

46. Leary, G.; Newman, R.; Morgan, K., Holzforschung 40:267(1986).

47. Chaing, V.; Funaoka, M.; Wang, X., TAPPI Pulping Conf., Proc. Book 1, Washington D. C., 1987:197.

48. Chiang, V.; Funaoka, M., Holzforschung 42:385(1988).

49. Yamasaki, T.; Hosoya, S.; Chen, C-L.; Gratzl, J.; Chang. H-m., Ekman Days, International Symp. on Wood and Pulping Chem., Vol. 2, Stockholm, 1981:34.

50. Kringstad, K.; Cheng, C., Tappi 52:2382(1969).

51. Koshijima, T.; Yaku, F.; Tanaka, R., Appl. Polym. Symp. 28:1025(1976).

52. Eriksson, O.; Lindgren, B., Svensk Papperstidn. 80:59(1977).

53. Jiang, J.; Chang, H-m.; Bhattacharjee, S.; Kwoh, D., TAPPI R&D Conf. Proc., Raleigh, NC, 1986:7.

54. Isogai, A.; Ishizu, A.; Nakano, J., J. Wood Chem. Technol. 7:311(1987) and 7:463(1987).

55. Taneda, H.; Nakano, J.; Hosoya, S.; Chang, H-m., J. Wood Chem. Technol. 7:485(1987).

56. Kleinert, T., Holzforschung 19:179(1965).

57. Iverson, T.; Wännström, S., Holzforschung 40:19(1986).

58. Minor, J., J. Wood Chem. Technol. 6:185(1986).

59. Szabo, A.; Goring, D., Tappi 51:440(1968).

60. Yan, J.; Johnson, D., J. Appl. Polym. Sci. 26:1623(1981).

61. Wilder, H.; Daleski, E., Tappi 47:270(1964) and 48:293(1965).

62. Nakano, J.; Schuerch, C., J. Am. Chem. Soc. 82:1677(1960).

63. Backman, A., Finn. Paper Tim. J. 13:200(1946).

64. Hartler, N.; Östberg, K., Svensk Papperstidn. 62:524(1959).

65. Larocque, G.; Maass, O., Can. J. Res. 15B:89(1937).

66. Schuerch, C., Ind. Eng. Chem., Prod. Res. Dev. 4:61(1965).

67. Morcellet-Sauvage, J.; Loucheux, C., Die Makromol. Chem. 176:315(1975).

68. Fuoss, R.; Watanabe, M.; Coleman, B., J. Polym. Sci. 48:5(1960).

69. Dooley, K.; Williams, J.; Gates, B.; Albright, A., J. Catal. 74:361(1982).

70. Pals, D.; Hermans, J., Rec. Trav. Chim. 71:513(1952).

71. Bernhard, S.; Hammett, L., J. Am. Chem. Soc. 75:1798(1953).

72. Affrossman, S.; Murray, J., J. Chem. Soc. (B) :579(1968).

73. Connors, W.; Kirk, T.; Brunow, G., TAPPI For. Biol. Wood Chem. Conf., Atlanta, TAPPI, 1973:163-7.

74. Apfeld, P. The Design, Preparation, Characterization, and Preliminary Reactions of an Insoluble Lignin Model. Doctoral Diss., The Institute of Paper Chemistry, Appleton, WI, 1986. 80p.

75. Bovee, M. The Synthesis and Characterization of a Polymer-supported Cellulose Model. Doctoral Diss., The Institute of Paper Chemistry, Appleton, WI, 1986. 128p.; and some unpublished results concerning the stability of model-to-polymer benzyl ether linkages.

76. Goring, D., Pulp Paper Mag. Can. 64:T517(1963).

77. Deratani, A.; Maraldo, T.; Darling, D.; Fréchet, J., Reactive Polymers 9:19(1988).

78. Daly, W., Makromol. Chem. Suppl. 2:3(1979).

79. Mathur, N.; Narang, C.; Williams, R. Polymers as Aids in Organic Chemistry, New York, Academic Press, 1980:15-18.

80. Klein, J.; Widdecke, H.; Bothe, N., Makromol Chem. Suppl. 6:211(1984).

81. Kun. K.; Kunin, R., Polym. Lett. 2:587(1964) and J. Polym. Sci. Part A-1 6:2689(1968).

82. Regen, S., J. Am. Chem. Soc. 96:5275(1974) and 97:3108(1975).

83. Lehn, D., Rohm and Haas Co., Personal communication concerning Amberlite XE-305; Polysciences Inc., Preliminary Data Sheet Amberlite XE-305, Warrington, PA.

84. Warshawsky, A.; Kalir, R.; Patchornik, A., J. Org. Chem. 43:3151(1978).

85. Warshawsky, A.; Kalir, R.; Desche, A.; Berkovitz, H.; Patchornik, A., J. Am. Chem. Soc. 101:4249(1979).

86. Heitz, W., Advances in Polymer Science 23:1(1977).

87. Rodriguez, O.; Setínek, K., J. Catal. 39:449(1975).

88. Data Sheet, Biobeads SM Adsorbents, Bio-Rad Laboratories, Richmond, CA.

89. Guyot, A.; Bartholin, M., Prog. Polym. Sci. 8:277(1982).

90. Relles, H.; Schluenz, R., J. Am. Chem. Soc. 96:6469(1974).

91. Miller, J.; Nunn, M., Tetrahedron Lett. 31:2691(1974).

92. Snyder, R.; Angelici, R.; Meck, R., J. Am. Chem. Soc. 94:2660(1972).

93. Sherrington, D. In Polymer-supported Reactions in Organic Synthesis. P. Hodge and D. Sherrington (Eds.), New York, J. Wiley & Sons, 1980: (a) Appendix and (b) 169-70.

94. March, J. Advanced Organic Chemistry, Reactions, Mechanisms, and Structure. 3rd ed., New York, McGraw-Hill Book Co., 1985: (a) 315, (b) 1028-32, (c) 17, and (d) 136.

95. Olah, G.; Tolgyesi, W. In Friedel-Crafts and Related Reactions. Vol. 2, G. Olah (Ed.), New York, Wiley-Interscience, 1964:659-784.

96. Bootsma, J.; Eling, B.; Challa, G., Reactive Polymers 3:17(1983).

97. Bacquet, M.; Caze, C.; Laureyns, J.; Bremard, C., Reactive Polymers 9:147(1988).

98. Pepper, K.; Paisley, H.; Young., M., J. Chem. Soc. :4097(1953).

99. Fréchet J.; Farrall, M. In Chemistry and Properties of Crosslinked Polymers. S. Labana (Ed.), New York, Academic Press, 1977:59-65.

100. Belfer, S.; Glozman, R.; Deshe, A.; Warshawsky, A., J. Appl. Polym. Sci. 25:2241(1980).

101. Williamami, S.; Le Maguer, D.; Caze, C., Reactive Polymers 6:213(1987).

102. Albright, R., Reactive Polymers 4:155(1986).

103. Halász, I.; Vogtel, P., Angew. Chem. Int. Ed. Engl. 19:24(1980).

104. Halász, I.; Martin, K., Angew. Chem. Int. Ed. Engl. 17:901(1978).

105. Hancock, W.; Prescott, D.; Vagelos, P.; Marshall, G., J. Org. Chem. 38:774(1973).

106. Letsinger, R.; Kornet, M.; Mahadevan, V.; Jerina, D., J. Am. Chem. Soc. 86:5163(1964).

107. Garland, C.; James, F.; Nelson, P.; Wallis, A., Appita 40:116(1987).

108. Larocque, G.; Mass, O., Can. J. Res. 19B:1(1941).

109. Wilson, G.; Proctor, A., Pulp Paper Mag. Can. 71:T483(1970).

110. Gustafson, R., Tappi 71(4):145(1988).

111. Farrall, M.; Fréchet, J., J. Org. Chem. 41:3877(1976).

112. Helferich, B., Adv. Carbohydr. Chem. 3:79(1948).

113. Fréchet, J.; Nuyens, L., Can. J. Chem. 54:926(1976).

114. Taylor, E.; McKillop, A., Acc. Chem. Res. 3:338(1970).

115. Whitehurst, D., Chem. Tech :44(1980).

116. Weinshenker, N.; Crosby, G.; Wong, J., J. Org. Chem. 40:1966(1975).

117. Fyles, T.; Leznoff, C., Can. J. Chem. 54:935(1976).

118. Evans, D.; Phillips, L.; Barrie, J.; George, M., J. Polym. Sci., Polym. Chem. Ed. 12:199(1974).

119. Bachmann, W., Org. Synth., Coll. Vol. III :841(1955).

120. Jiawei, C.; Zhang-Huang, X.; Jianzong, L.; Shiyan, C., Reactive Polymers 6:334(1987).

121. Apfeld, P.; Bovee, L.; Barkhau, R.; Dimmel, D., J. Wood Chem. Technol. 8:483(1988).

122. Greene, T. Protective Groups in Organic Chemistry. New York, Wiley-Interscience, 1981: (a) 296, (b) 31, and (c) 97.

123. Dimmel, D., The Institute of Paper Chemistry, Unpublished results, 1987.

124. Barkhau, R.; Malcolm, E.; Dimmel, D., J. Wood Chem. Technol. Submitted, 1989.

125. Oikawa, Y.; Yoshioka, T.; Yonemitsu, O., Tetrahedron Lett. 23:885(1982).

126. Corey, E.; Danheiser, R.; Chandrasekaran, S.; Siret, P.; Keck, G.; Gras, J.-L., J. Am. Chem. Soc. 106:8031(1978).

127. Zeifel, G.; Brown, H., Org. Reactions 13:1(1963).

128. Corey, E.; Suggs, J., J. Org. Chem. 33:3224(1973).

129. Gent, P.; Gigg, R., J. C. S. Chem. Comm. :277(1974).

130. Gigg, J.; Gigg, R.; Payne, S.; Conant, R., J. Chem. Soc. Perkin Trans. I :244(1987).

131. Van Cleve, J.; Russell, C., Carb. Res. 25:465(1972).

132. Ford, W.; Mohanraj, S.; Periyasamy, M., Br. Polym. J. 16:179(1984).

133. Ford, W.; Balakrishnan, T., Macromol. 14:284(1981).

134. Ford, W.; Yacoub, S., J. Org. Chem. 46:819(1981).

135. Shapiro, M., J. Org. Chem. 41:3197(1976).

136. Lonsky, W., Kimberly Clark Corp., Personal communication, 1987.

137. Zuber, G.; Staiger, D.; Warren, R., Anal. Chem. 55:64(1983).

138. Antonsson, T.; Moberg, C., Reactive Polymers 8:113(1988).

139. Fuji, K.; Ichikawa, K.; Node, M.; Fujita, E., J. Org. Chem. 44:1661(1979).

140. Kartha, K.; Dasgupta, F.; Singh, P.; Srivastava, H., J. Carb. Chem. 5:437(1986).

141. Olah, G.; Narang, S., Tetrahedron 38:2225(1982).

142. Jung, M.; Lyster, M., J. Org. Chem. 42:3761(1977).

143. Kaiser, E.; Tam, J.; Kubiak, T.; Merrifield, R., Tetrahedron Lett. 29:303(1988).

144. Jung, M.; Ornstein, P., Tetrahedron Lett. 21:2659(1980).

145. Jung, M.; Lyster, M., Org. Synth. 59:35(1980).

146. Bundy, G.; Peterson, D., Tetrahedron Lett. 18:41(1978).

147. Akelah, A., Synthesis :413(1981).

148. Crowley, J.; Rapoport, H., Acc. Chem. Res. 9:135(1976).

149. Farrall, M.; Fréchet, J., J. Am. Chem. Soc. 100:7998(1978).

150. Collman, J.; Reed, C., J. Am. Chem. Soc. 95:2048(1973).

151. Crowley, J.; Harvey III, T.; Rapoport, H., J. Macromol. Sci. Chem. 7:1118(1973).

152. Scott, L.; Rebek, J.; Ovsyanko, L.; Sims, C., J. Am. Chem. Soc. 99:625(1977).

153. Darling, G.; Fréchet, J., J. Org. Chem. 51:2270(1986).

154. Fréchet, J.; Schuerch, C., Carbohyd. Res. 22:399(1972).

155. Montanari, F.; Tundo, P., J. Org. Chem. 46:2125(1981) and 47:1298(1982).

156. Sugii, A.; Ogawa, N.; Nozaki, Y.; Haratake, M., Reactive Polymers 8:3(1988).

157. Ajayaghosh, A.; Pillai, V., J. Org. Chem. 52:5714(1987).

158. Cole, J.; Johnson, W.; Robins, P.; Walker, J., J. Chem. Soc. :244(1962).

159. Troughton, G., Holzforschung 26:170(1972).

160. Yeddanapalli, L.; Francis, D., J. Makromol. Chem. 55:74(1962).

161. Dimmel, D.; Bovee, L., The Institute of Paper Chemistry, Unpublished results, 1986.

162. Hosoya, S.; Kanazawa, K.; Kaneko, H.; Nakano, J., J. Japan Wood Res. Soc. 26:118(1980).

163. Dimmel, D.; Shepard, D., J. Wood Chem. Technol. 2:297(1982).

164. Holshouser, M.; Kolb, M., J. Pharm. Sci. 75:619(1986).

165. Ferrari, G.; Casagrande, C., Chim. Ind. 43:621(1961). Chem. Abst. 56:8626h(1962).

166. Nonni, A. The Reactions of Hydrogen Peroxide and Oxygen with Lignin Model Dimers of the 1,2-Diaryl-1,3-Propanediol Type Structure. Doctoral Diss., SUNY College of Environmental Science and Forestry, Syracuse, NY, 1982.

167. Omori, S.; Dence, C., Wood Sci. Technol. 15:67(1981).

168. Gierer, J.; Noren, I., Holzforschung 34:197(1980).

169. Adler, E.; Gierer, J., Acta Chem. Scand. 9:84(1955).

170. Gierer, J.; Acta Chem. Scand. 8:1319(1954).

171. Gigg, R.; Warren, C., J. Chem. Soc., Sect. C :1903(1968).

172. Farhangi, Y.; Graddon, D., Aust. J. Chem. 26:983(1973).

173. Airoldi, C.; Silva, M.; Chagas, A., J. Chem. Soc. Dalton Trans. 9:1913(1986).

174. Stewart, J.; Young, J. Solid Phase Peptide Synthesis. San Francisco, W. H. Freeman and Co., 1969:Appendix 28.

175. Yoon, B.-H.; Okada, M.; Yasuda, S.; Terashima, N., J. Japan Wood Res. Soc. 25:302(1979).

176. Dimmel, D.; Schuller, L., J. Wood Chem. Technol. 6:535(1986).

177. Dr. Gary Turner, Spectral Data Services, 818 Pioneer, Champaign, IL, 61820.

178. Perrin, D.; Armarego, L.; Perrin, D. Purification of Laboratory Chemicals, 2nd ed. New York, Pergamon Press, 1980. 586p.

179. Reed, G. Nucleophilicity of Hydroxide, Hydrosulfide, and Anthrahydroquionone Ions Toward Saturated and Unsaturated Carbon Centers at High Temperatures. Doctoral Diss., The Institute of Paper Chemistry, Appleton, WI, 1988. 135p.

180. Apfeld, P.; Dimmel, D., J. Wood Chem. Technol. 8:461(1988).

181. E. Millard, The Degradation of Selected 1,5-Anhydroalditols by Molecular Oxygen in Alkaline Media. Doctoral Diss., The Institute of Paper Chemistry, Appleton, WI, 1976. 159p.

182. Dimmel, D.; The Institute of Paper Chemistry, Personal communication, 1988.

183. Silverstein, R.; Bassler, G.; Morrill, T. Spectrometric Identification of Organic Compounds. 4th ed. New York, John Wiley & Sons, 1981:3-93.

184. The ^{1}H-NMR specrum was recorded in $CDCl_3$ and $CDCl_3/D_2O$ by Dr. Jerrold Lokensgard on a 60 MHz instrument at Lawrence University, Appleton, WI, 1987.

185. Riegel, B.; Witcoff, H., J. Am. Chem. Soc. 68:1913(1946).

186. Melius, M., The Institute of Paper Chemistry, Unpublished results, 1986.

APPENDIX 1

POLYMER-SUPPORTED BENZYL IODIDE HYDROLYSIS DATA

Table 7. Iodine loss vs. time at temperature data for the hydrolysis of iodomethylated macroreticular polystyrene (3) in 1.00M NaOH.

Time (Seconds)	Iodine Loading (mmol/g) 130 °C	150 °C	171 °C
00000	3.09	3.09	3.09
01800	-----	2.99	2.52
03600	3.03	-----	-----
05400	-----	2.87	1.40
07200	2.94	-----	-----
09000	-----	2.59	0.80
10800	2.89	-----	-----
14400	-----	2.33	0.54

The pseudo first order kinetic equation took the following form:[75]

$$\ln R = -k't + \ln R_0 \qquad [14]$$

where R = concentration of iodine (mmol/g)
R_0 = initial concentration of iodine (mmol/g)
t = seconds at temperature
k' = $k[^-OH]$ which is assumed to be constant

Table 8. Values of k' (sec^{-1}) determined from a plot of ln R vs. t; R^2 values are also shown.

Temperature °C	k' (sec -1)	- R2
130	6.67×10^{-6}	0.993
150	1.98×10^{-5}	0.990
171	1.27×10^{-4}	0.977

The activation energy was calculated from the Arrhenius equation by determining the slope of a plot of ln k' vs. 1/T (°K):

$$k' = Ae(-E/RT) \qquad [15]$$

where E = activation energy
A = frequency factor
R = gas constant
T = absolute temperature

$$\text{slope} = -12{,}557 = -E/R; \quad r^2 = -0.973$$

$$(E/R) \times R = E$$

$$\text{then } E = 12{,}557 \times (1.987 \times 10^{-3}) = 25.0 \text{ kcal/mol}$$

APPENDIX 2

HETEROGENEOUS BENZYL ETHER HIGH TEMPERATURE STABILITY DATA

Two separate trials, one at 169 °C and the other at 171 °C, were conducted with supported guaiacylpropanol (**6**) in 1.00M NaOH to determine the stability of the heterogeneous benzyl ether linkage. Both the amount of guaiacylpropanol (GPOH) cleaved into solution and the quantity remaining on the resin were measured. The loading value of the untreated model was 1.29 mmol/g.

Table 9. The reaction temperature for the first half of the stability test was 169 °C.

Time (Hours)	Soluble GPOH (mmol/g)	Resin GPOH (mmol/g)	Mass Bal. (% vs. 1.29)
1	0.12	0.93	81.4
1	0.11	0.99	85.3
2	0.14	0.90	80.6
2	0.14	0.89	79.8
3	0.09	0.92	76.7
3	0.14	0.83	75.2
4	0.12	0.89	78.3
4	0.10	0.82	71.3
5	0.11	0.85	74.4
5	0.12	0.85	75.2
6	0.10	0.82	71.3
6	0.11	0.81	71.3

Table 10. The reaction temperature for the second half of the stability test was 171 °C.

Time (Hours)	Soluble GPOH (mmol/g)	Resin GPOH (mmol/g)	Mass Bal. (% vs. 1.29)
0.5	0.14	0.92	82.2
0.5	0.16	0.91	82.9
1.5	0.16	0.87	79.8
1.5	0.17	0.83	77.5
2.5	0.14	0.75	69.0
2.5	0.14	0.80	72.9
3.5	0.14	0.89	79.8
3.5	0.15	0.81	74.4
4.5	0.12	0.72	65.1
4.5	0.13	0.75	68.2
5.5	0.13	0.73	66.7
5.5	0.12	0.75	67.4

APPENDIX 3

CONDENSATION REACTION RATE DATA

Table 11. Data from a control cook of syringyl alcohol (**72**) at 150 °C in 1.00M NaOH.

	mmols ($\times 10^{-3}$)				
Time (Minutes)	Syringyl Alcohol	Syringol	4-methyl-syringol	Syring-aldehyde	Disyringyl-methane
000	20.03	0.00	0.00	0.00	0.00
030	13.69	0.54	0.26	0.23	2.43
030	13.66	0.53	0.19	0.20	2.43
060	11.11	0.90	0.51	0.41	3.72
060	10.89	0.93	0.57	0.42	3.80
090	8.95	1.17	0.67	0.53	5.06
090	9.13	1.18	0.76	0.50	5.08
120	7.40	1.35	1.26	0.54	5.87
180	5.28	1.54	1.04	0.57	5.76
180	5.65	1.53	0.68	0.58	6.42
240	4.12	1.68	0.91	0.78	6.91
240	4.27	1.73	1.02	0.56	6.60

Table 12. Data from a homogeneous cook of syringyl alcohol (**72**) with guaiacylpropane (**4**) at 150 °C in 1.00M NaOH. The yields of guaiacylpropane and C5-Cα dimer (**8**) follow in Table 13.

	mmols ($\times 10^{-3}$)				
Time (Minutes)	Syringyl Alcohol	Syringol	4-methyl-syringol	Syring-aldehyde	Disyringyl-methane
000	20.02	0.00	0.00	0.00	0.00
030	12.36	0.34	0.94	0.19	1.94
030	12.20	0.35	0.81	0.16	1.97
060	7.87	0.58	1.32	0.30	2.99
060	8.96	0.63	0.98	0.30	2.90
090	6.97	0.83	0.98	0.30	3.45
090	6.88	0.84	1.09	0.32	3.65
120	5.32	0.96	1.43	0.30	4.20
120	5.34	0.98	1.39	0.33	3.93
180	3.31	1.12	1.33	0.32	4.65
180	3.49	1.15	1.06	0.30	4.69
240	2.37	1.31	1.54	0.36	5.03
240	2.39	1.28	1.37	0.36	5.06

Table 13. Yields of guaiacylpropane (4) and C5-Cα dimer (8) from the homogeneous cook at 150 °C in 1.00M NaOH.

	mmols ($\times 10^{-3}$)	
Time (Minutes)	Guaiacyl-propane	C5-Cα dimer
000	20.00	0.00
030	18.50	2.57
030	18.40	2.43
060	15.64	3.82
060	17.01	3.73
090	16.40	4.64
090	16.40	4.90
120	15.77	5.75
120	15.85	5.46
180	14.27	6.44
180	15.12	6.28
240	14.46	7.21
240	14.50	7.21

Table 14. Data from a control cook of syringyl alcohol (**72**) at 170 °C in 1.00M NaOH.

Time (Minutes)	mmols ($\times 10^{-3}$) Syringyl Alcohol	Syringol	4-methyl-syringol	Syring-aldehyde	Disyringyl-methane
000	20.00	0.00	0.00	0.00	0.00
010	11.36	1.10	0.28	1.34	2.15
010	10.99	1.08	0.27	2.14	2.05
020	8.55	1.59	0.42	2.14	3.11
020	8.35	1.59	0.48	1.51	3.04
040	5.46	2.12	0.68	1.93	3.72
040	5.27	2.12	0.74	1.97	3.55
060	3.80	2.46	0.83	1.95	4.97
060	3.89	2.48	0.83	1.84	4.91
090	2.47	2.67	1.34	2.11	4.92
090	2.49	2.76	1.44	1.50	4.88
120	1.63	2.85	1.73	1.70	5.39
120	1.53	2.77	1.83	1.88	5.18

Table 15. Data from a homogeneous cook of syringyl alcohol (**72**) with guaiacylpropane (**4**) at 172 °C in 1.00M NaOH. The yields of guaiacylpropane and C5-Cα dimer (**8**) follow in Table 16.

	mmols ($\times 10^{-3}$)				
Time (Minutes)	Syringyl Alcohol	Syringol	4-methyl-syringol	Syring-aldehyde	Disyringyl-methane
000	20.00	0.00	0.00	0.00	0.00
010	8.73	3.26	----	2.00	2.19
010	7.62	3.18	----	2.37	1.94
020	5.06	3.33	----	3.17	2.80
020	4.94	3.46	----	2.76	2.74
040	2.36	3.76	----	3.44	3.16
040	2.36	3.85	----	3.52	3.01
060	1.22	3.87	----	3.49	3.27
060	1.16	3.59	1.11*	3.06	3.08
090	0.74	3.95	1.46	3.34	3.17
090	0.83	4.10	1.59	2.73	3.49
120	0.51	3.99	1.48	2.60	3.26
120	0.55	2.98	1.58	3.05	3.05

* The values reported are estimates; the chromatogram signal was not well resolved from that of the neighboring guaiacylpropane.

Table 16. Yields of guaiacylpropane (4) and C5-Cα dimer (8) from the homogeneous cook at 172 °C in 1.00M NaOH.

Time (Minutes)	mmols ($\times 10^{-3}$) Guaiacyl-propane	C5-Cα dimer
000	25.00	0.00
010	-----	4.86
010	-----	4.25
020	-----	6.53
020	-----	6.11
040	-----	7.74
040	-----	7.43
060	-----	8.21
060	18.67*	7.95
090	18.57	8.26
090	18.57	8.72
120	18.32	8.20
120	17.97	7.82

* The values reported are estimates; the chromatogram signal was not well resolved from that of the neighboring 4-methylsyringol (75).

Table 17. Data from a heterogeneous cook of syringyl alcohol (**72**) with polymer-supported guaiacylpropanol (**6**) at 170 °C in 1.00M NaOH. The yields of supported guaiacylpropanol and C5-Cα dimer (**10**) follow in Table 18.

	mmols ($\times 10^{-3}$)				
Time (Minutes)	Syringyl Alcohol	Syringol	4-methyl-syringol	Syring-aldehyde	Disyringyl-methane
000	20.00	0.00	0.00	0.00	0.00
010	9.65	1.06	1.28	1.85	1.71
010	8.97	1.04	1.20	2.79	1.60
010	8.63	1.08	1.15	2.52	1.29
020	5.90	1.44	1.80	2.54	1.98
020	5.94	1.46	1.66	2.41	2.12
020	5.98	1.55	1.86	2.69	1.95
040	2.57	1.72	2.35	2.37	1.90
040	2.82	1.83	2.49	3.07	2.21
040	3.09	1.86	2.44	2.73	2.44
060	1.72	2.06	3.18	2.52	2.43
060	1.70	1.90	3.16	2.47	2.17
060	1.89	2.01	3.04	2.81	1.91
090	1.10	2.20	3.54	3.03	2.49
090	1.26	2.04	3.98	1.59	2.31
120	0.83	2.11	3.64	1.75	2.29
120	1.03	2.39	4.43	2.13	2.82
120	1.09	2.19	3.63	2.65	2.26

Table 18. Yields of supported guaiacylpropanol (**6**) and C5-Cα dimer (**10**) from the heterogeneous cook at 170 °C in 1.00M NaOH.

Time (Minutes)	mmols ($\times 10^{-3}$) Guaiacyl-propanol	C5-Cα dimer
000	25.0	0.0
010	23.7	1.1
010	25.9	1.1
010	25.4	0.9
020	23.4	1.6
020	24.7	1.7
020	22.1	1.5
040	22.9	2.2
040	21.7	2.2
040	22.0	2.0
060	18.4	1.9
060	20.9	2.1
060	21.5	1.9
090	18.8	2.0
090	20.9	2.4
120	20.5	2.0
120	17.5	2.6
120	18.9	2.0

APPENDIX 4

SPECTRA OF SELECTED COMPOUNDS

Appendix 4 contains the NMR and FTIR spectra of selected soluble and insoluble compounds, respectively. The FTIR spectra were obtained as KBr pellets.

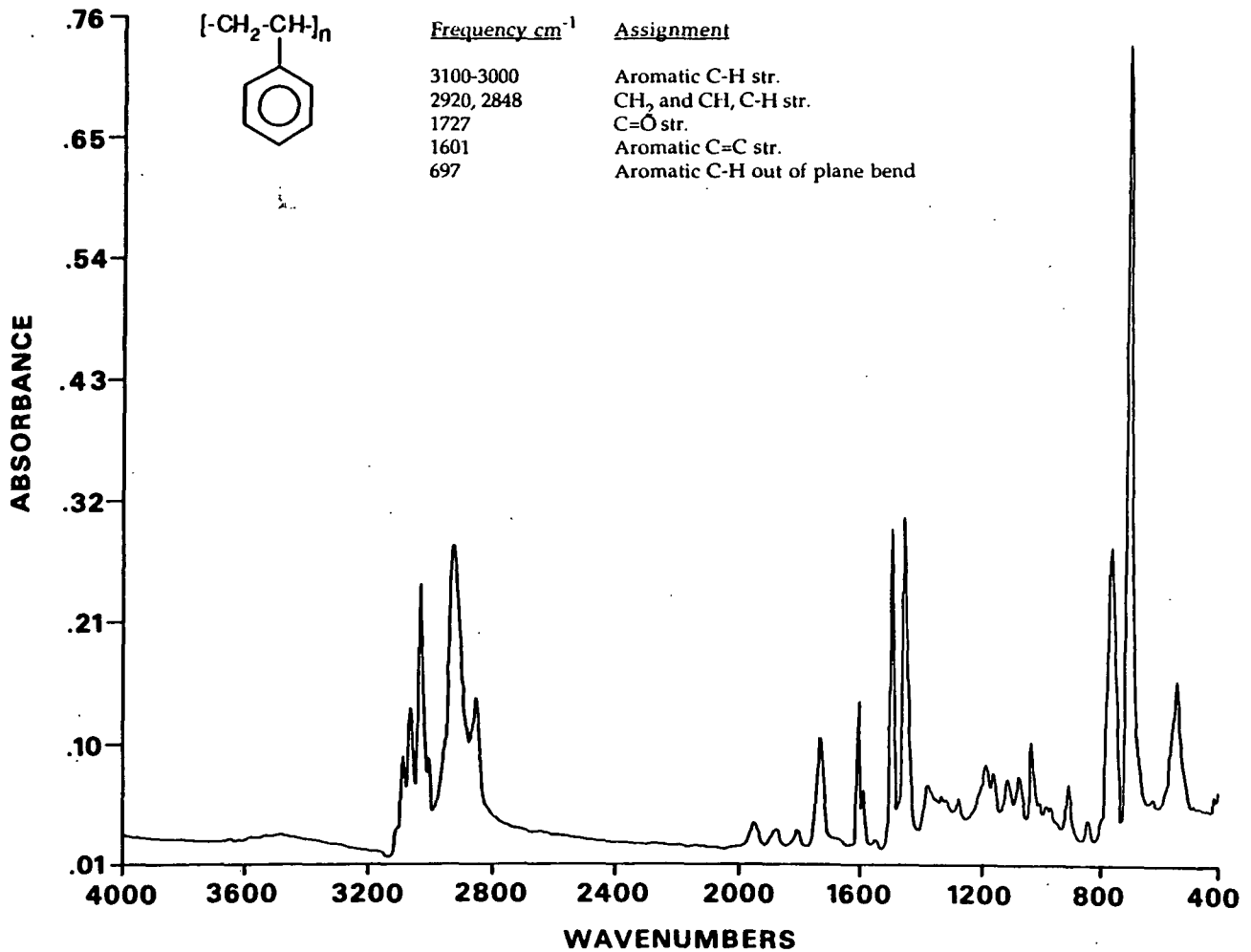


Figure 11. Infrared spectrum of Amberlite XE-305 (**1**).

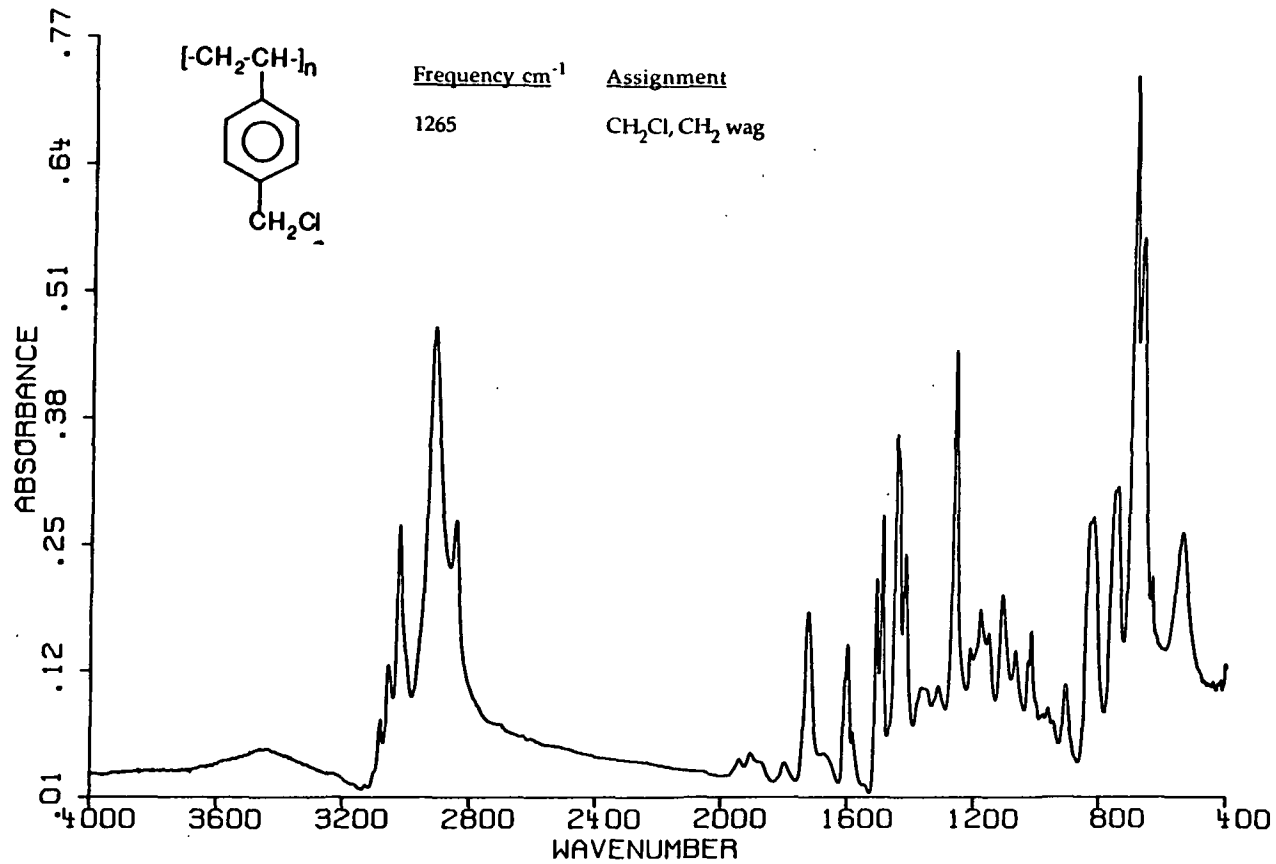


Figure 12. Infrared spectrum of chloromethylated Amberlite XE-305 (**2**).

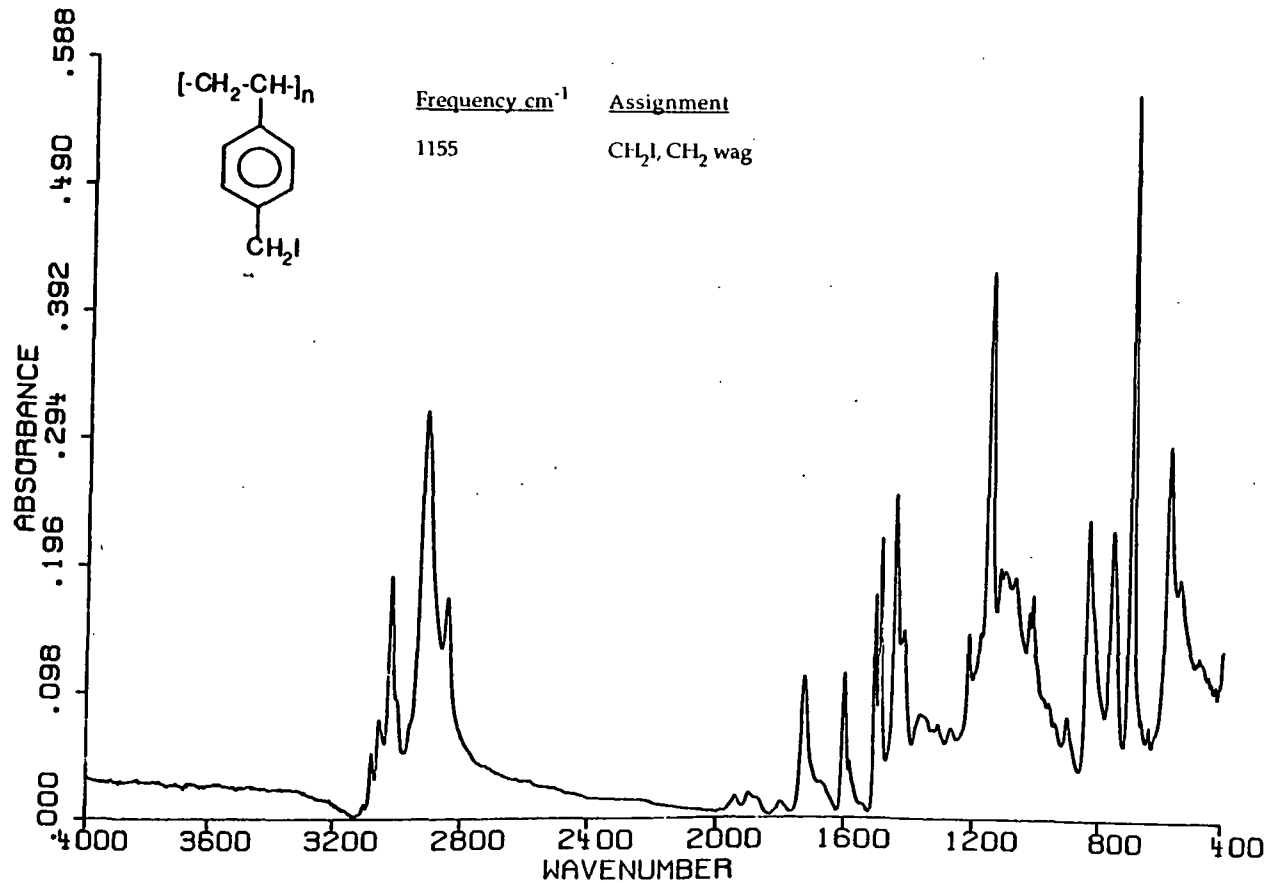


Figure 13. Infrared spectrum of iodomethylated Amberlite XE-305 (3).

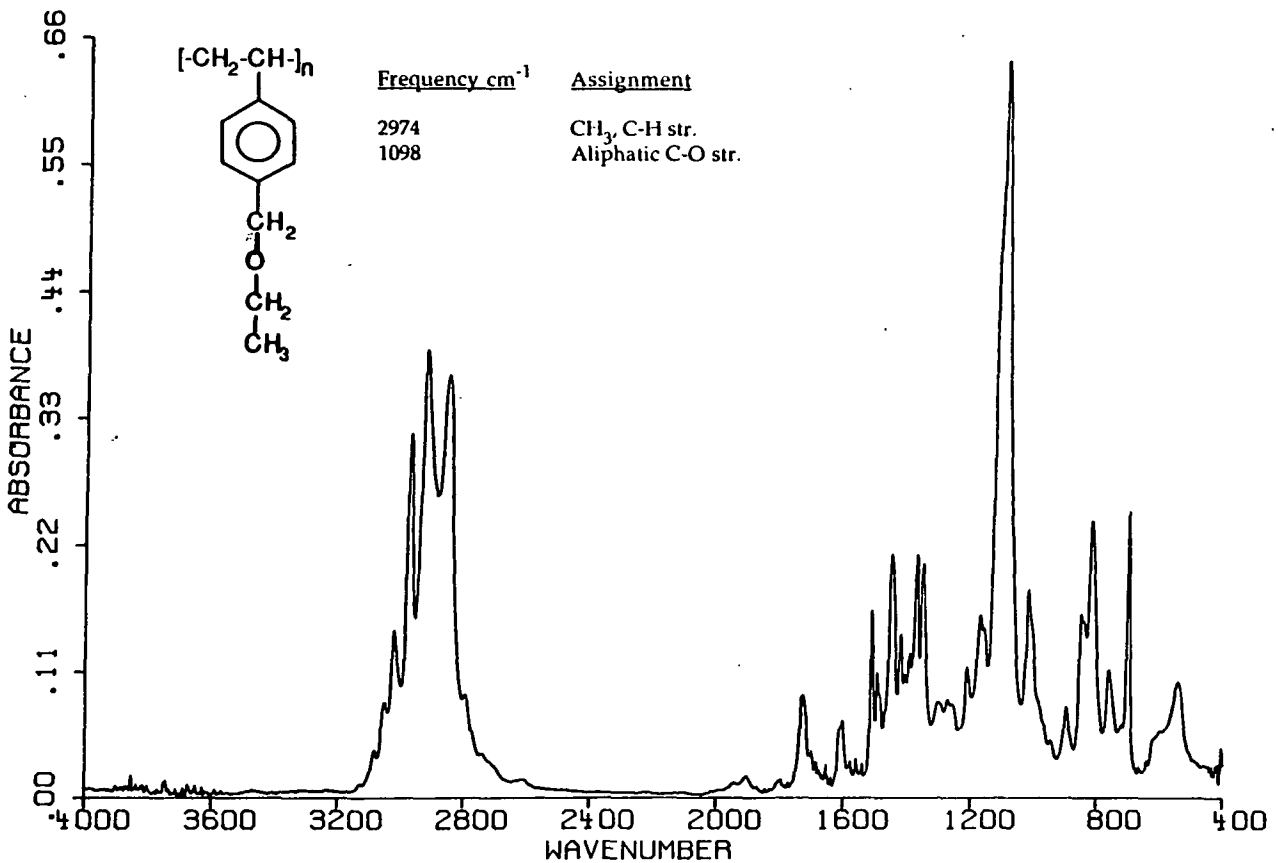


Figure 14. Infrared spectrum of polymer-supported benzyl ethoxide.

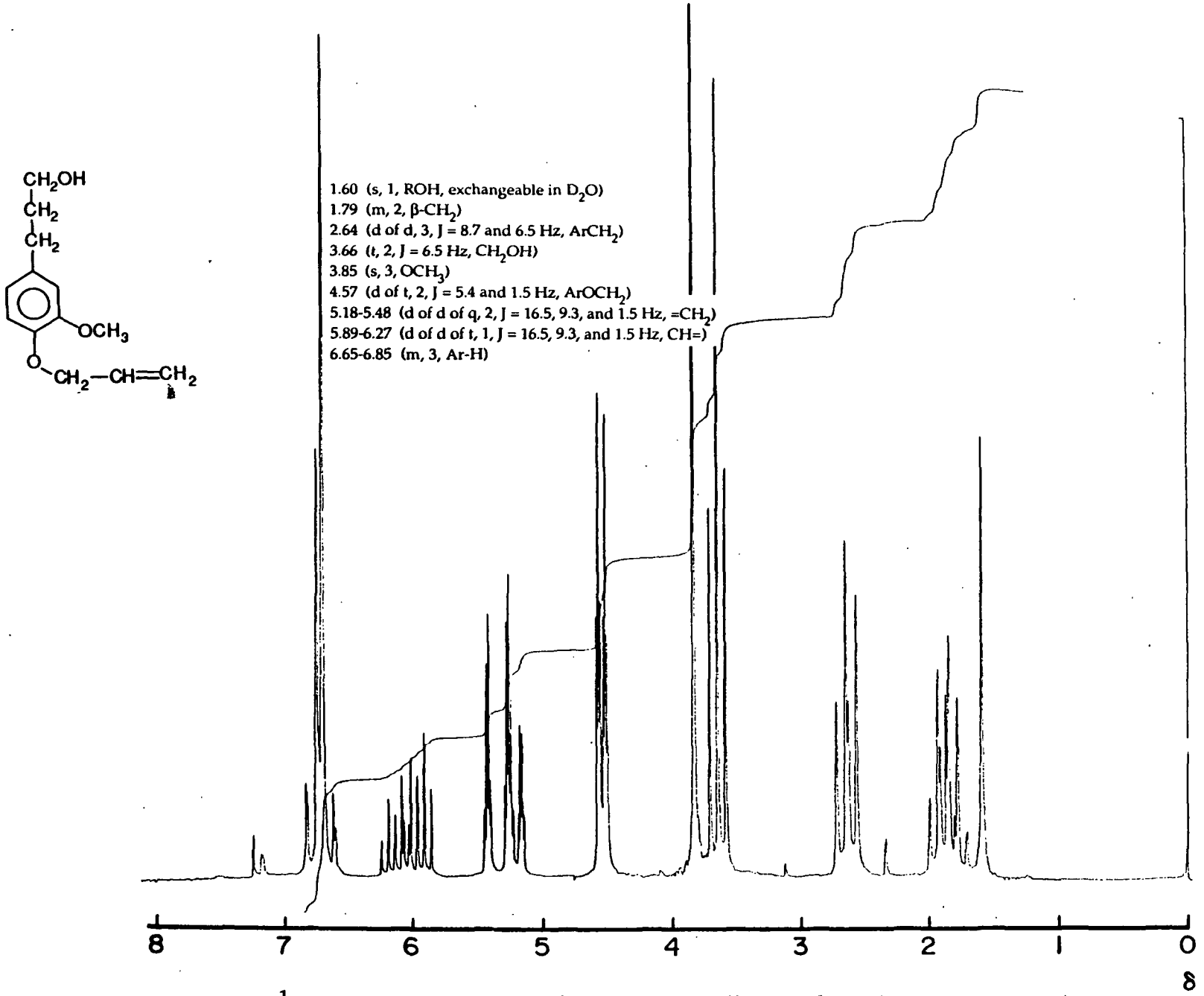


Figure 15. ^{1}H-NMR spectrum of 3-(3'-methoxy-4'allyloxyphenyl)propan-1-ol (25) in $CDCl_3$.

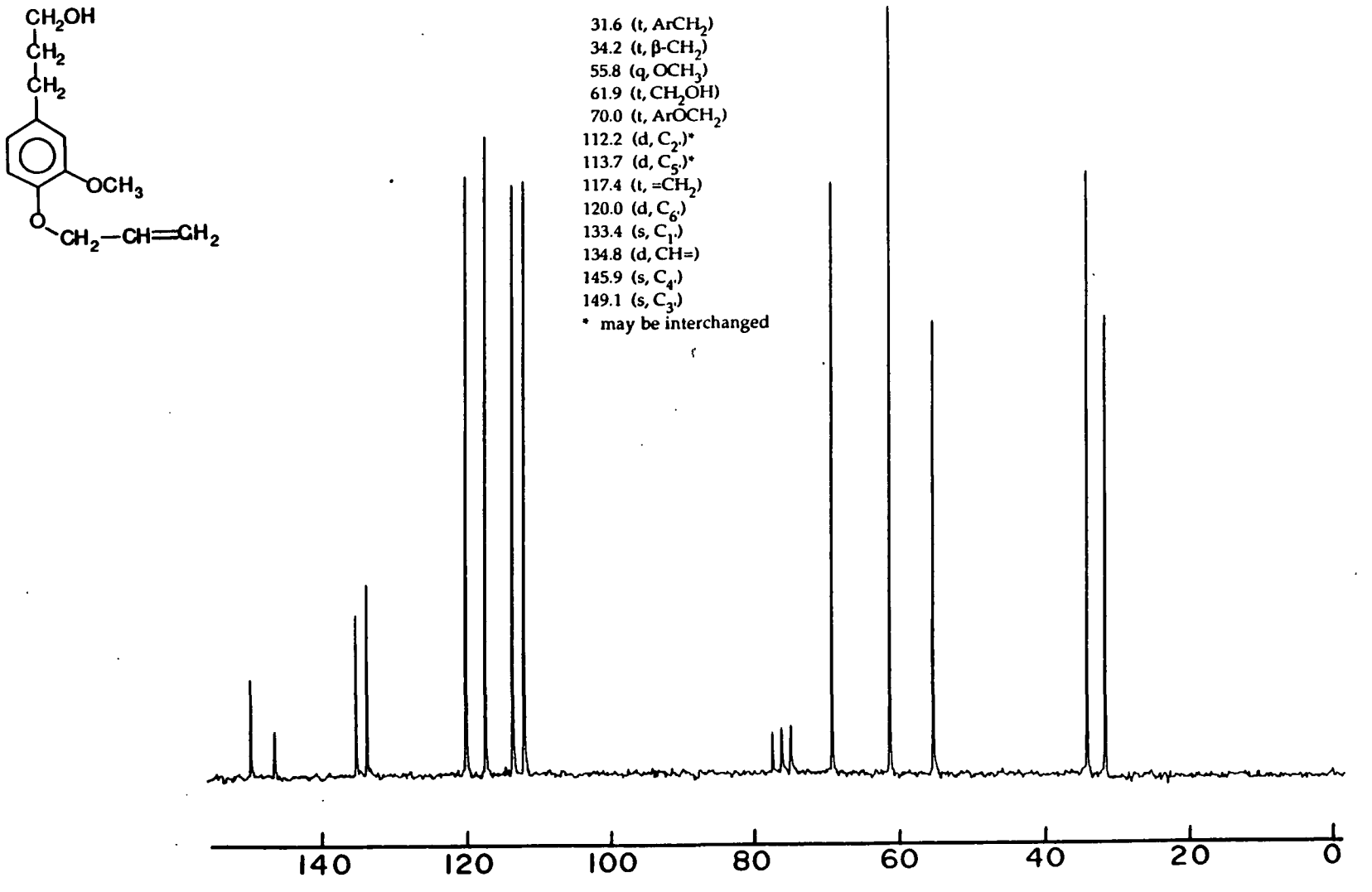


Figure 16. Decoupled ^{13}C-NMR spectrum of 3-(3'-methoxy-4'allyloxyphenyl)propan-1-ol (**25**) in $CDCl_3$.

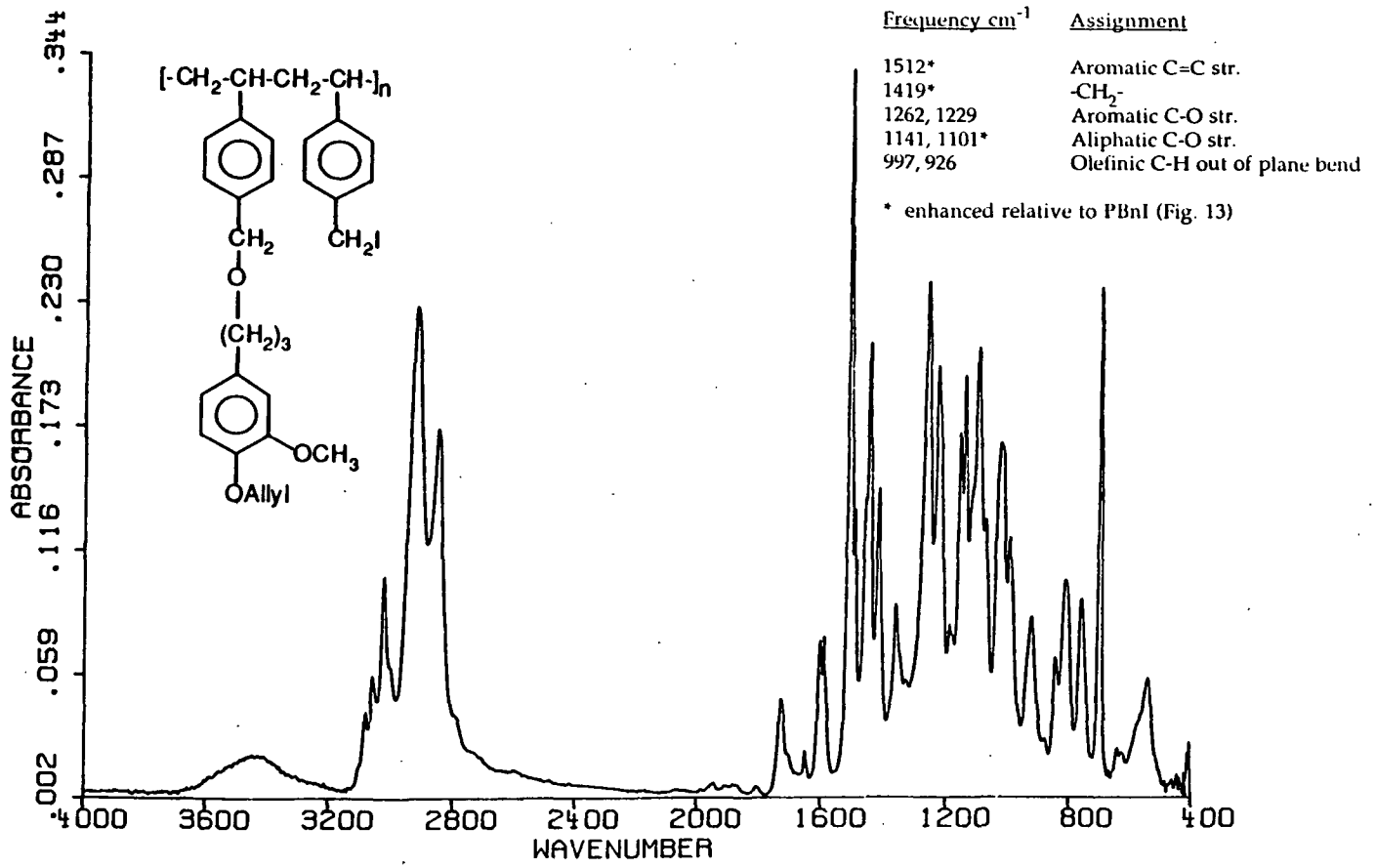


Figure 17. Infrared spectrum of polymer-supported allylguaiacylpropanol (27).

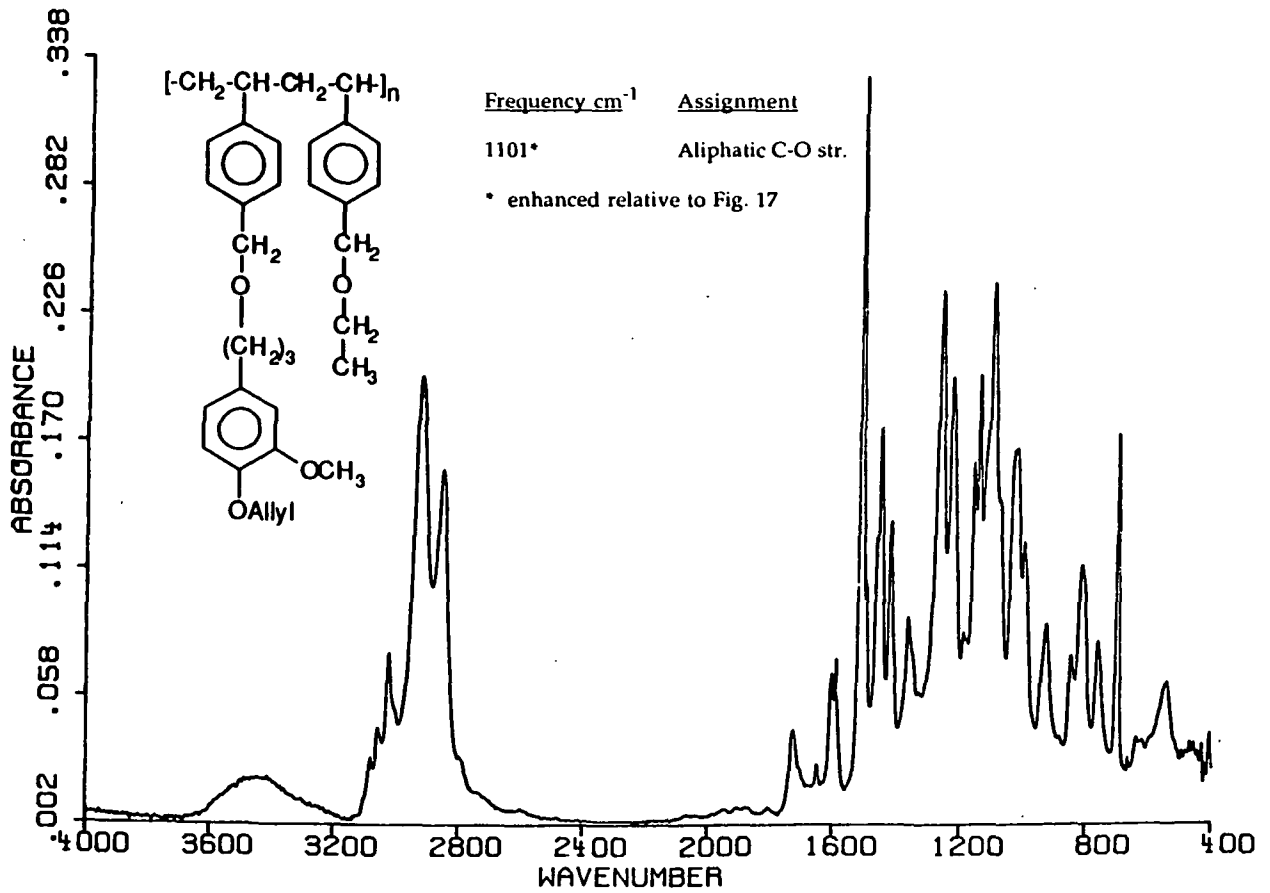


Figure 18. Infrared spectrum of polymer-supported allylguaiacylpropanol/ethoxide (28).

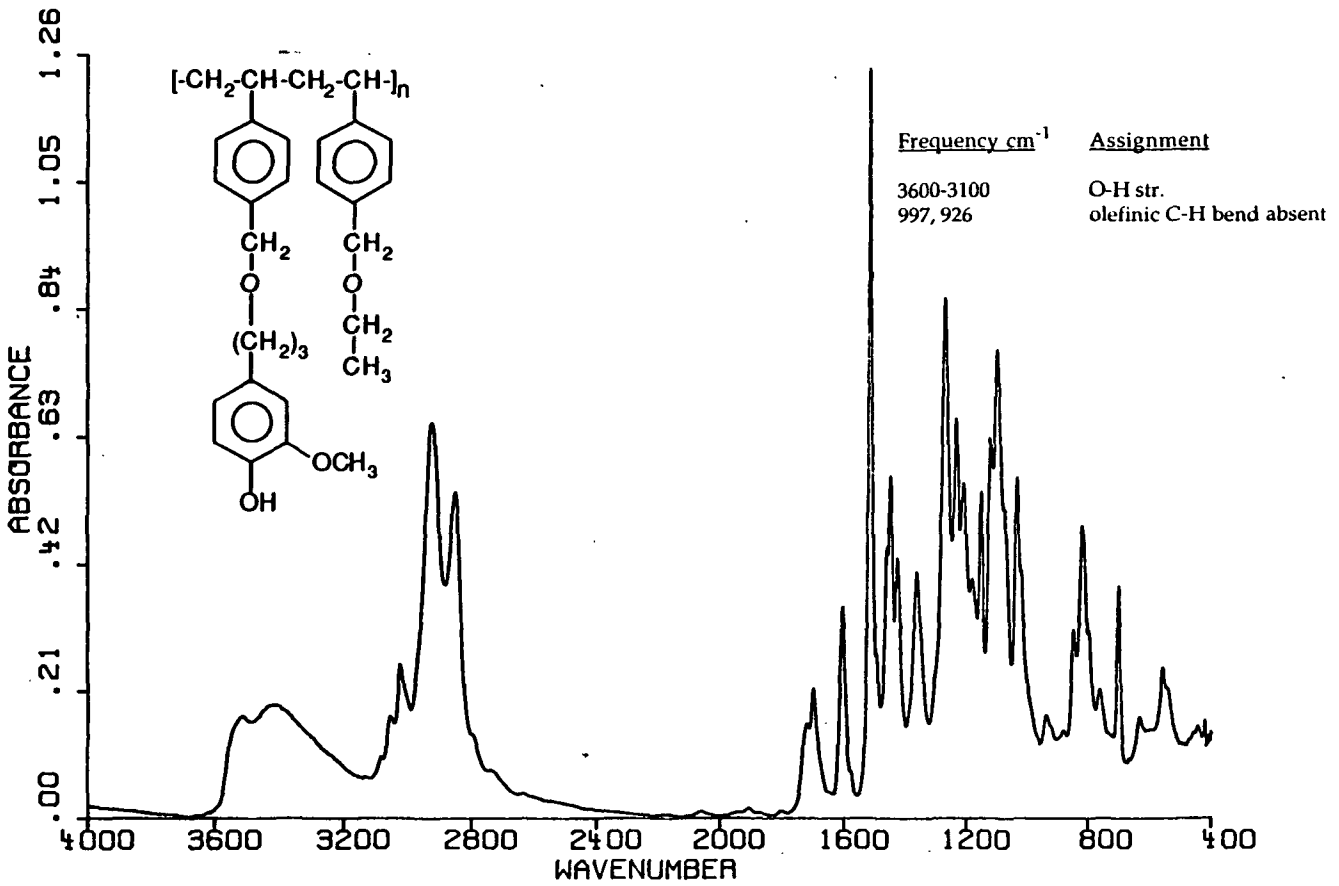


Figure 19. Infrared spectrum of polymer-supported guaiacylpropanol (6).

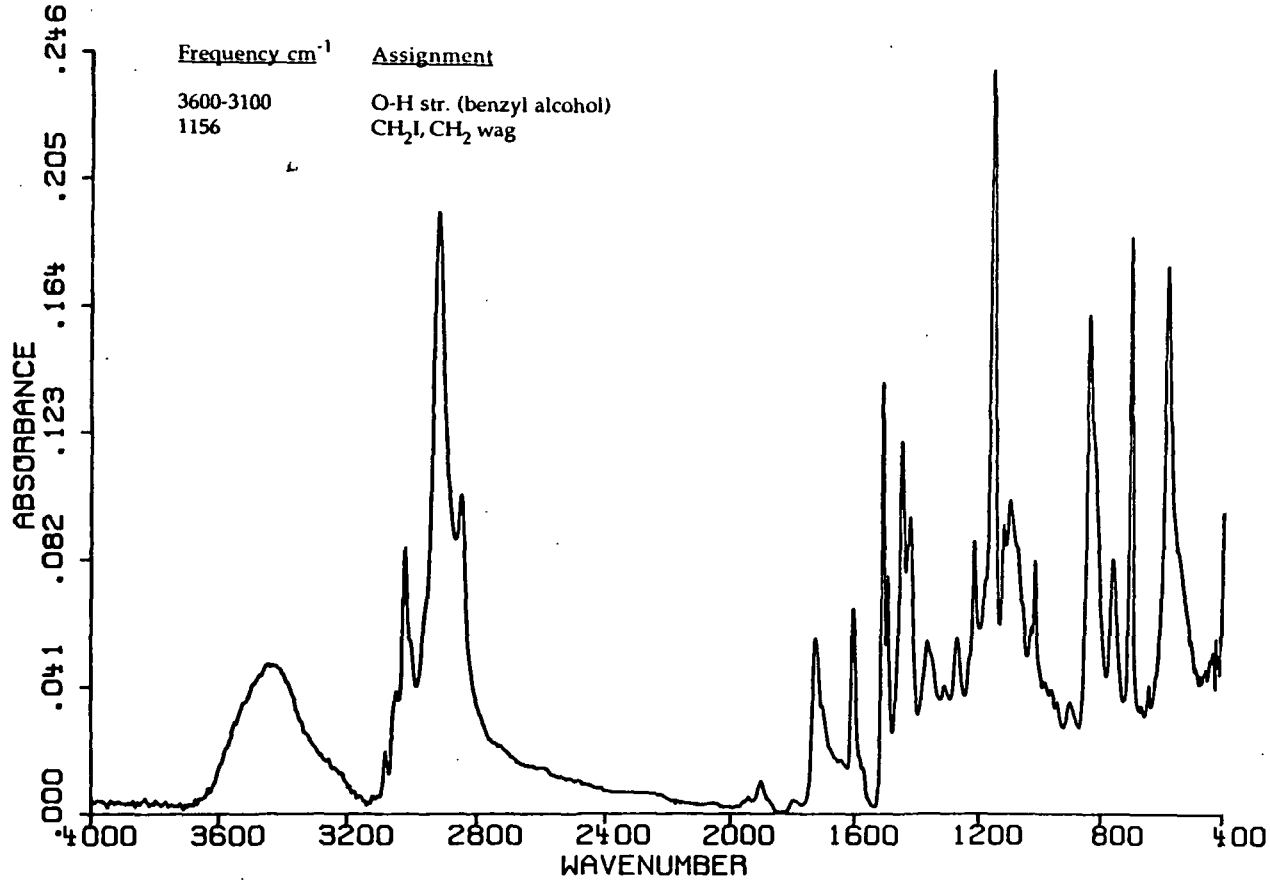


Figure 20. Infrared spectrum of **6** after treatment with iodotrimethylsilane.

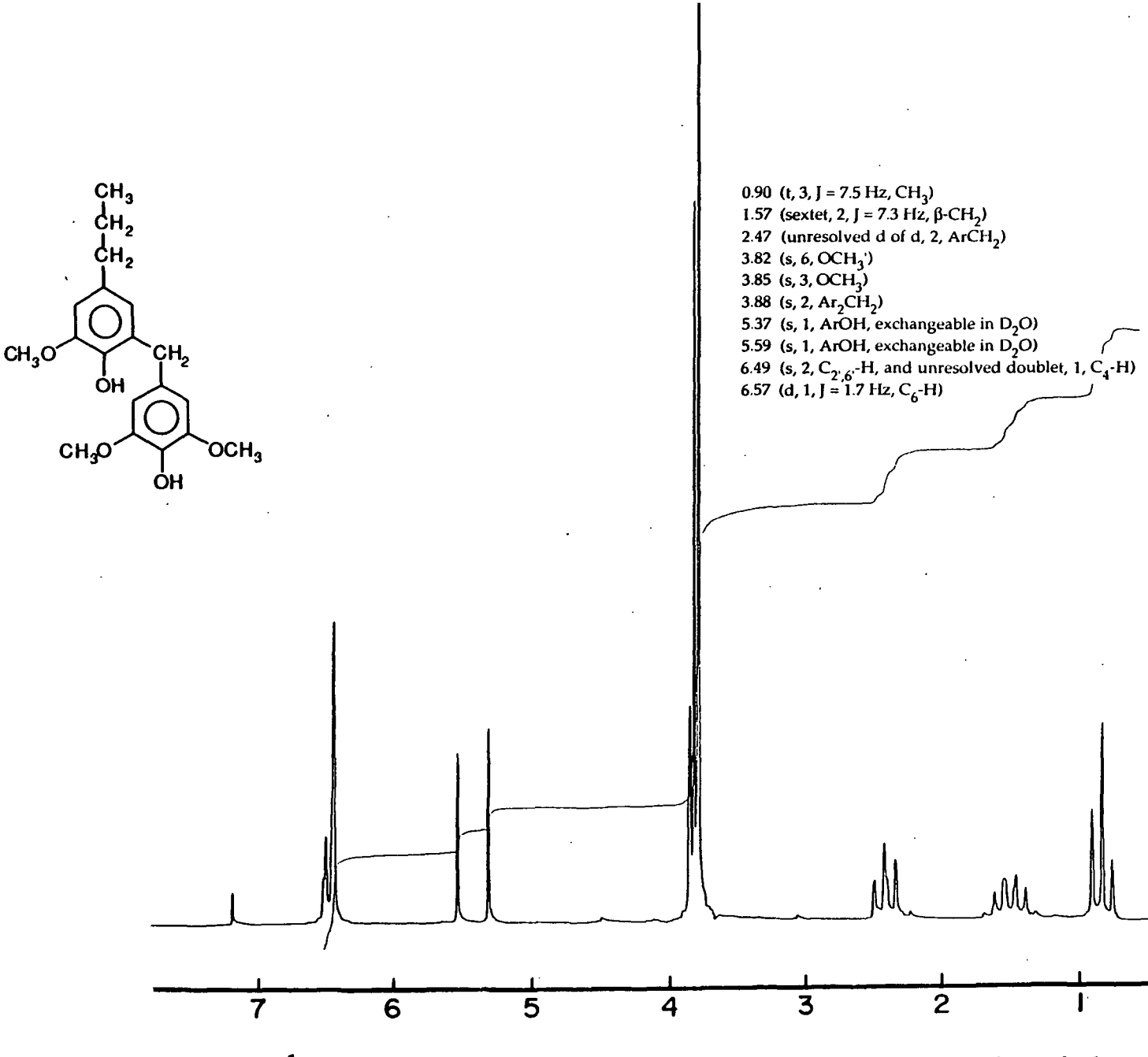


Figure 21. ^{1}H-NMR spectrum of 2,4'-dihydroxy-5-propyl-3,3',5'-trimethoxydiphenylmethane (8) in $CDCl_3$.

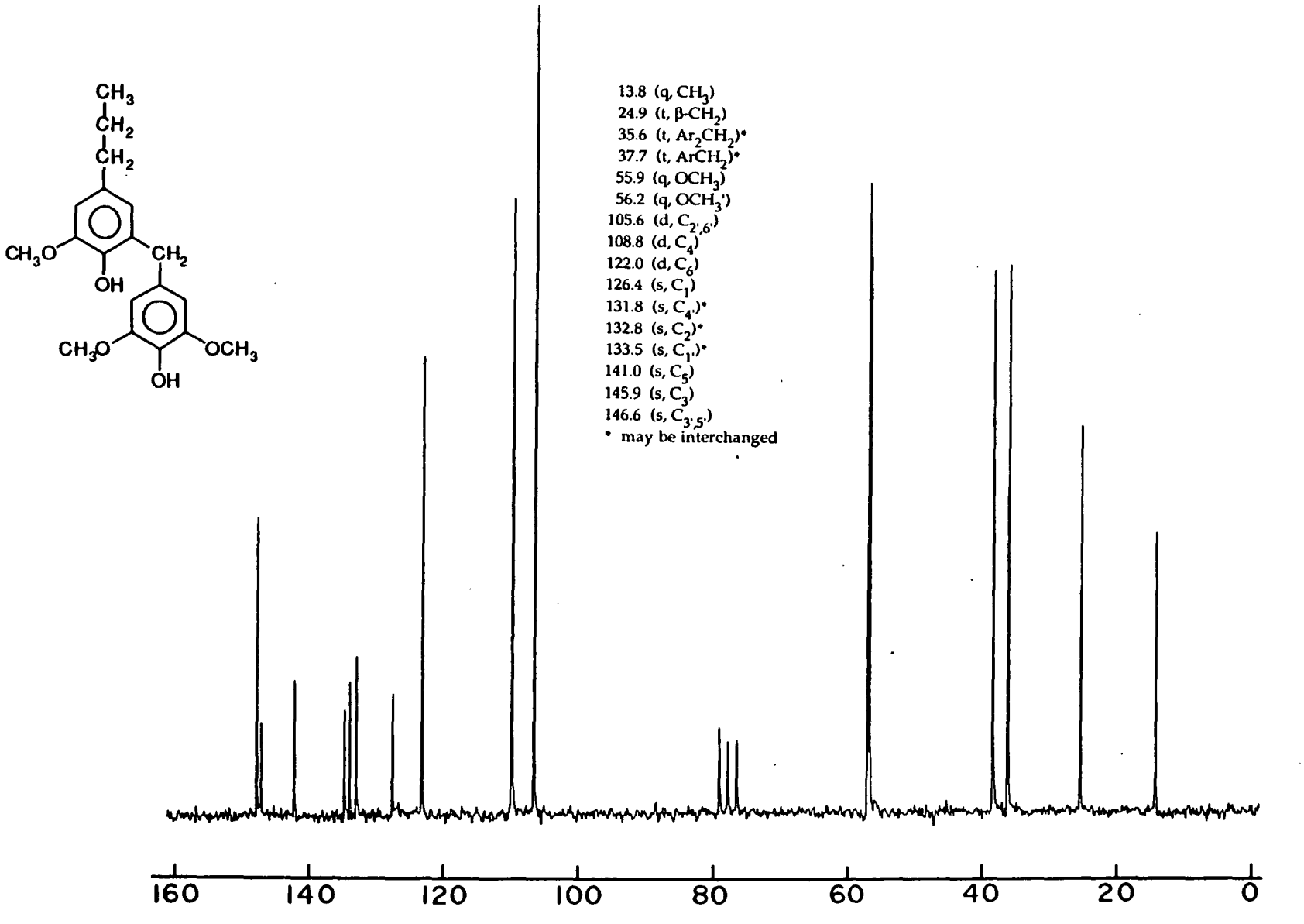


Figure 22. Decoupled ^{13}C-NMR spectrum of 2,4'-dihydroxy-5-propyl-3,3',5'-trimethoxydiphenylmethane (8) in $CDCl_3$.

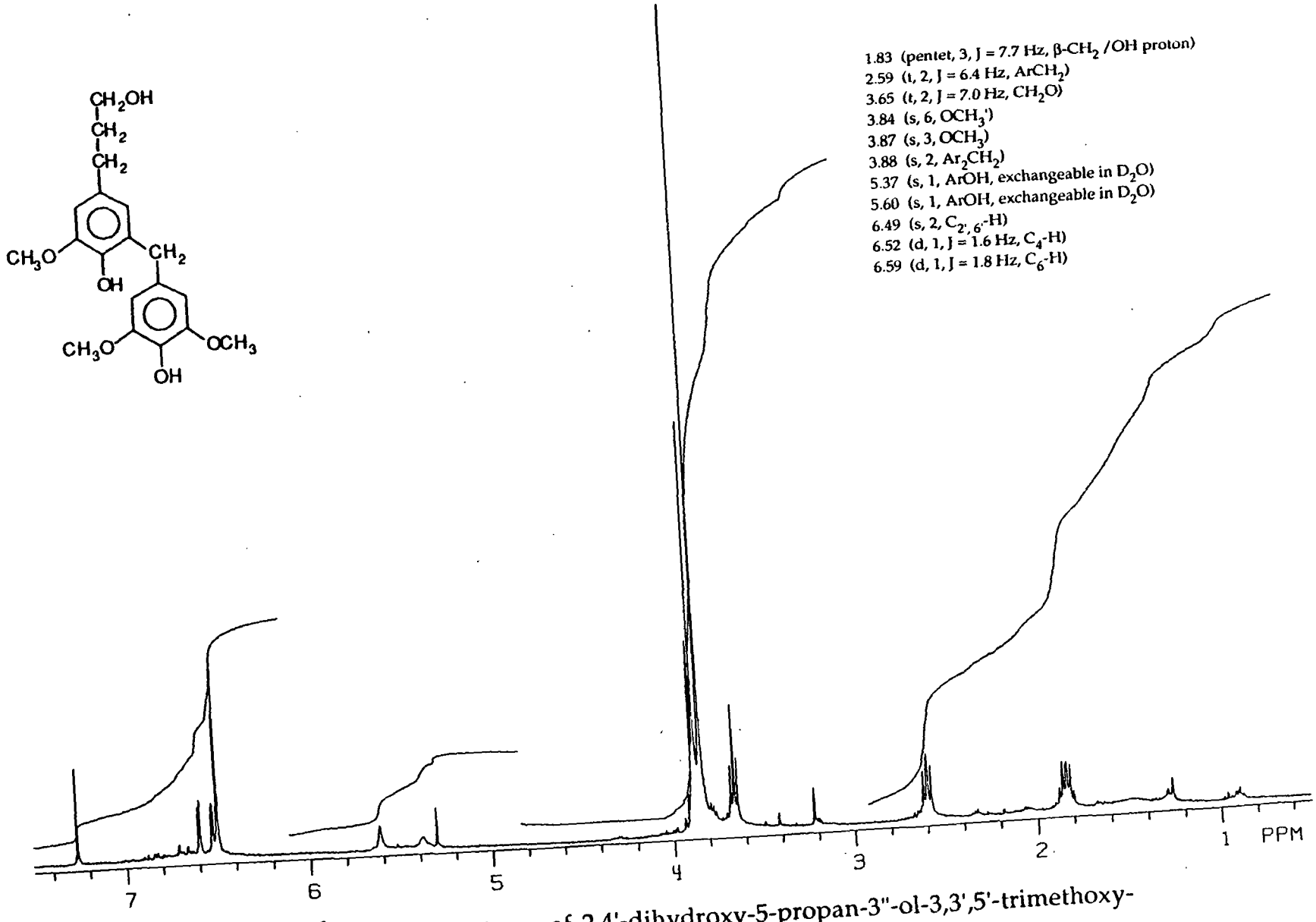


Figure 23. ^{1}H-NMR spectrum of 2,4'-dihydroxy-5-propan-3"-ol-3,3',5'-trimethoxy-diphenylmethane (77) in $CDCl_3$.

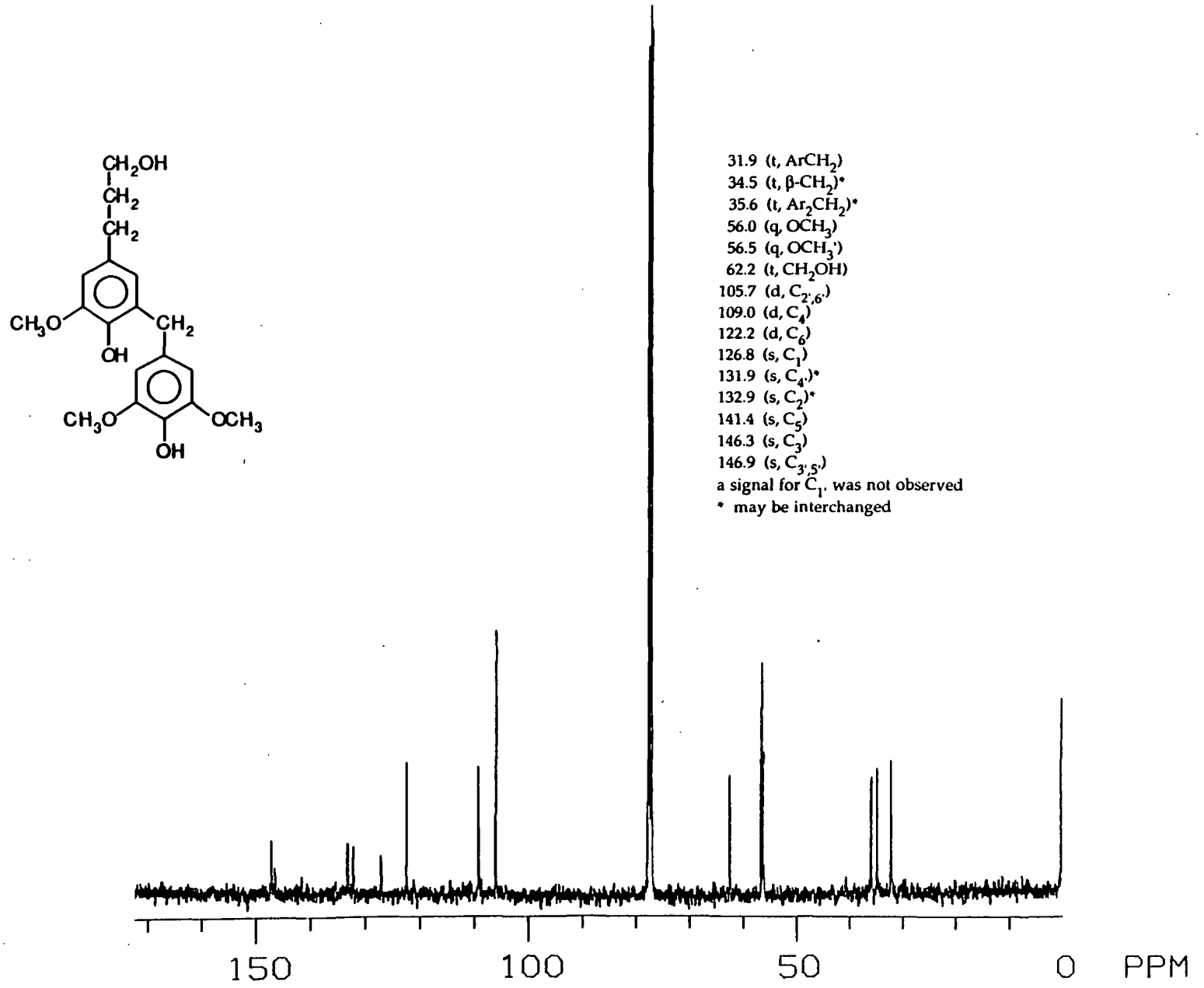


Figure 24. Decoupled ^{13}C-NMR spectrum of 2,4'-dihydroxy-5-propan-3"-ol-3,3',5'-trimethoxydiphenylmethane (77) in $CDCl_3$.

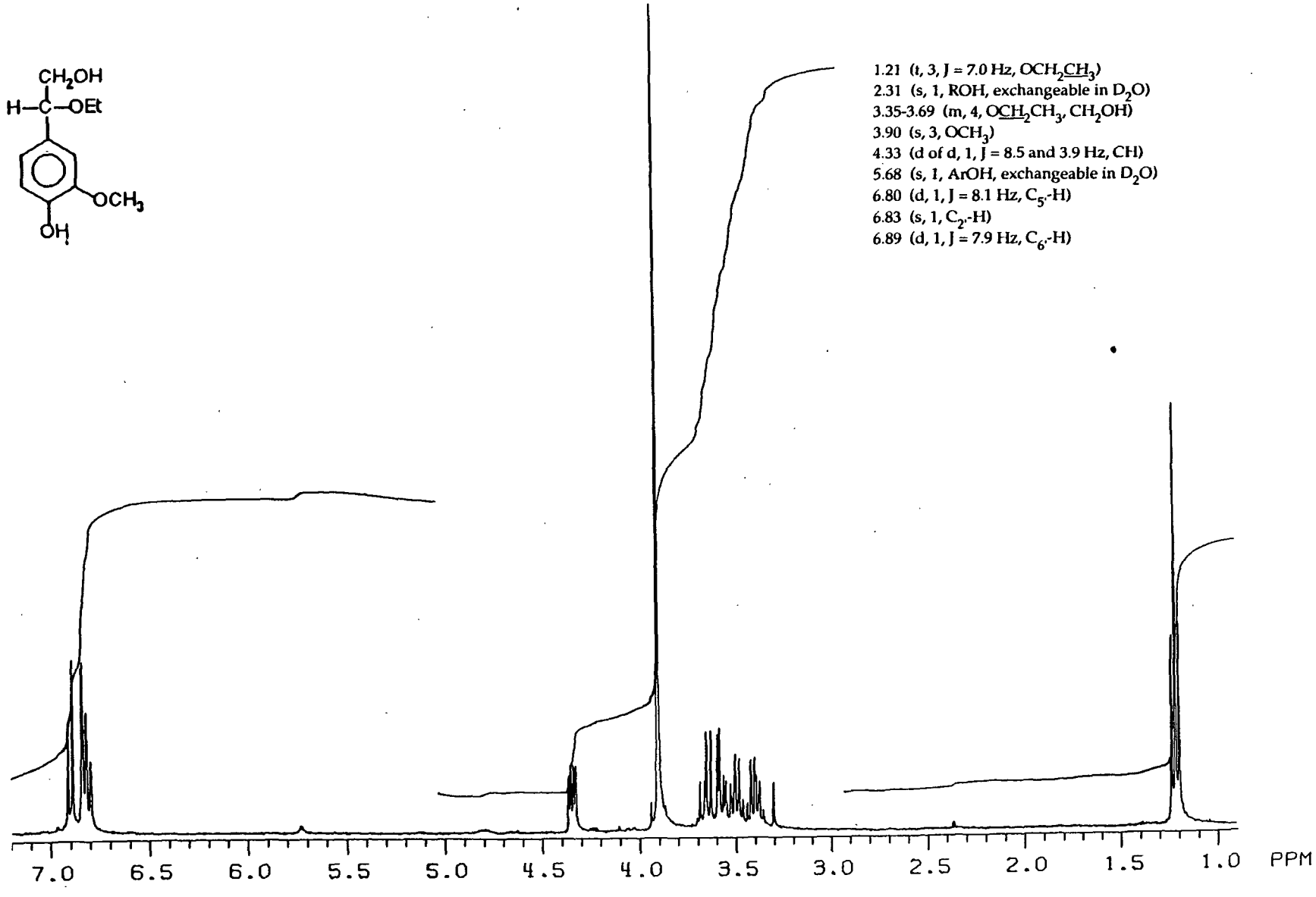


Figure 25. ^{1}H-NMR spectrum of 2-ethoxy-2-(3'-methoxy-4'-hydroxyphenyl)ethan-1-ol (**56**) in $CDCl_3$.

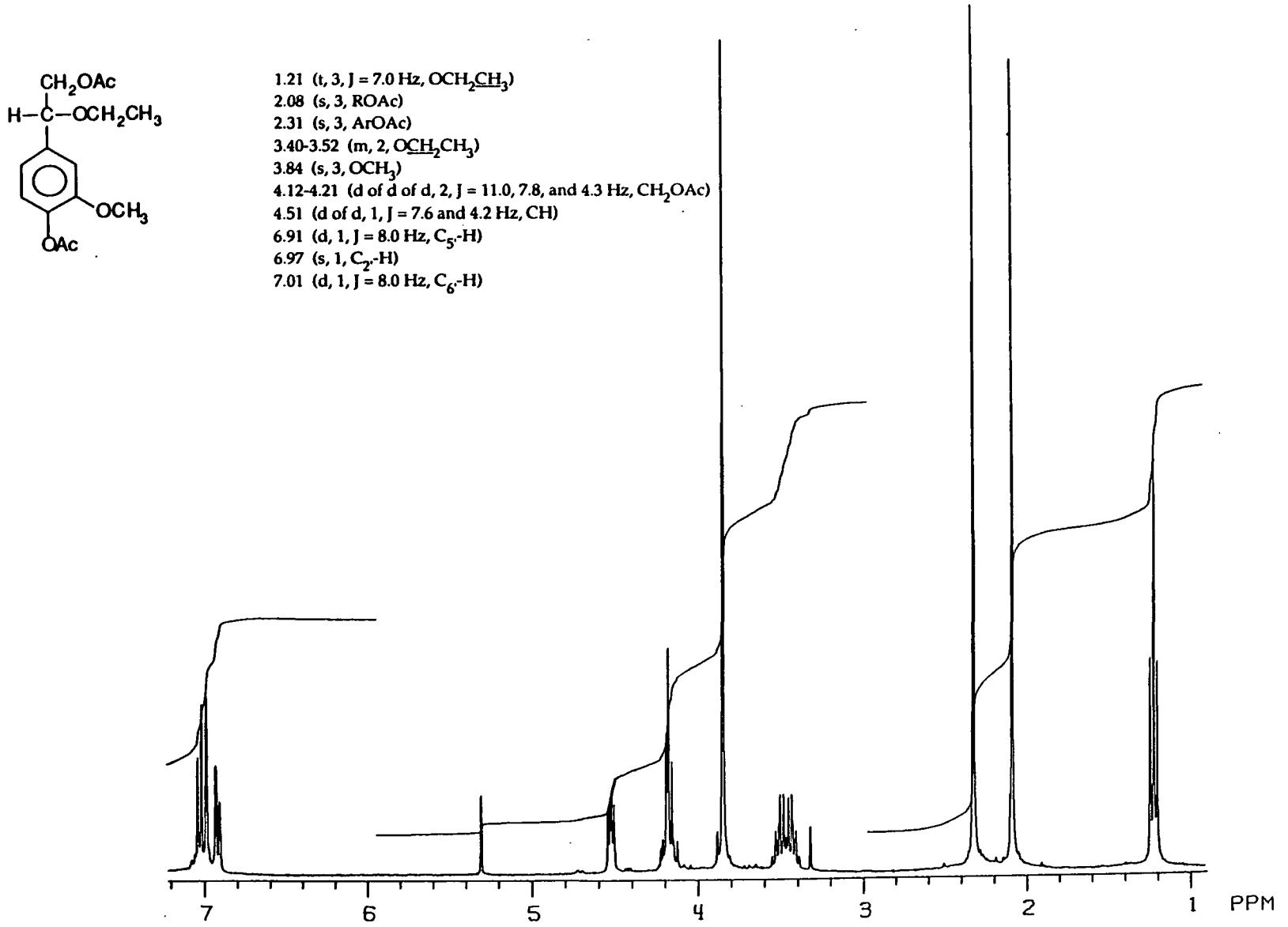


Figure 26. ^{1}H-NMR spectrum of 1,4'-diacetoxy-2-ethoxy-2-(3'-methoxyphenyl)-ethane **(61)** (acetylated **56**) in $CDCl_3$.

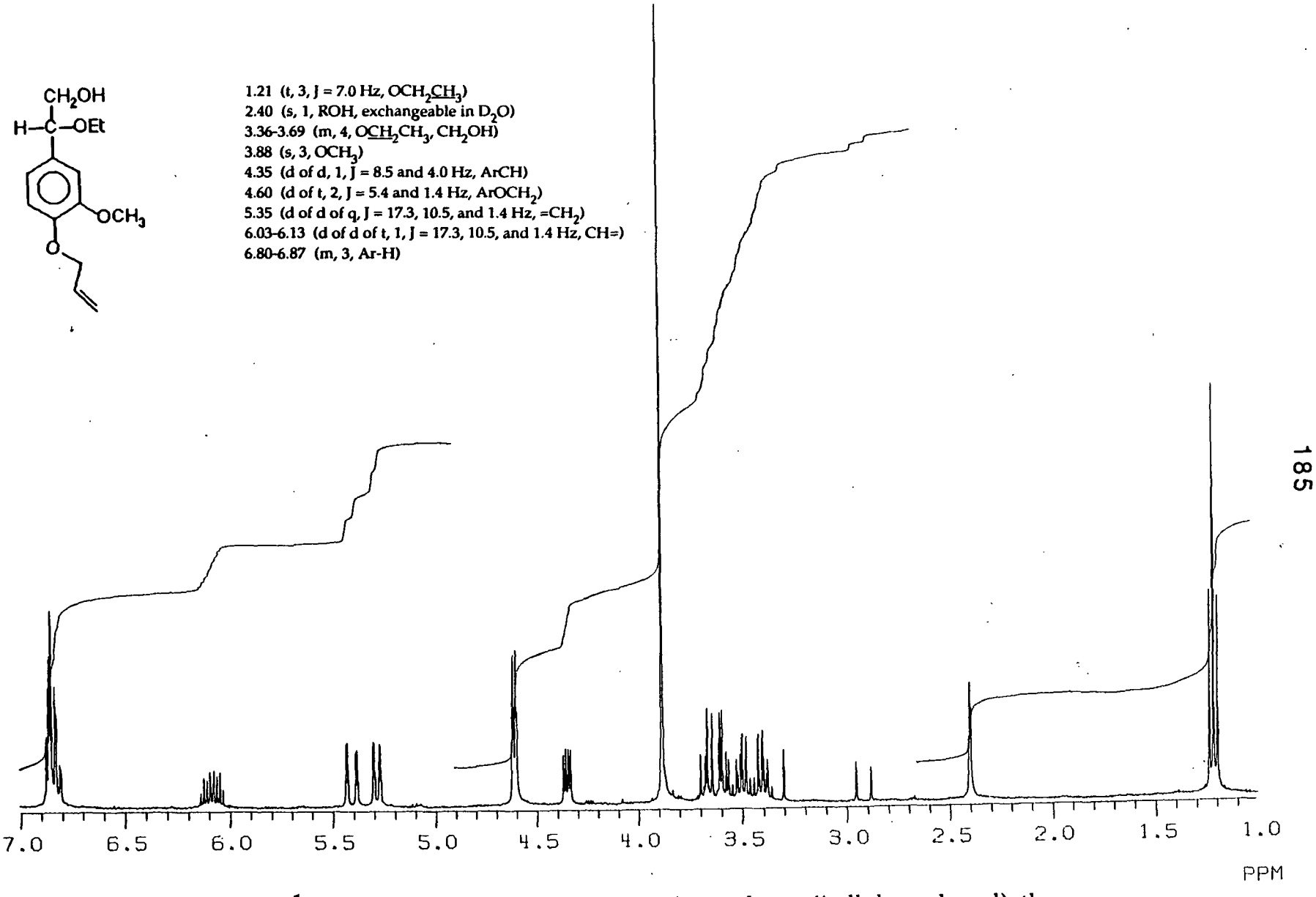


Figure 27. ^{1}H-NMR spectrum of 2-ethoxy-2-(3'-methoxy-4'-allyloxyphenyl)ethan-1-ol (47) in $CDCl_3$.

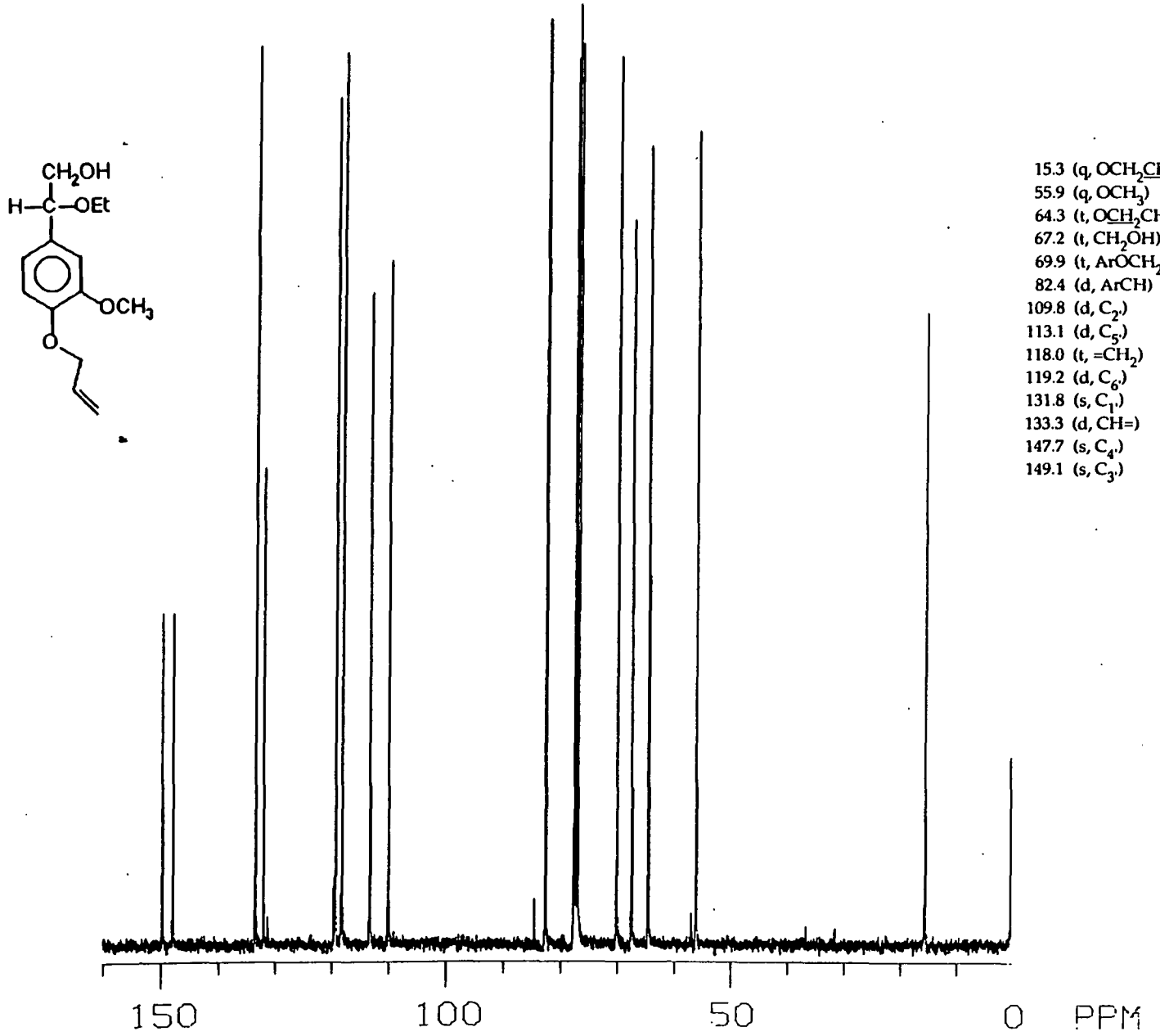


Figure 28. Decoupled ^{13}C-NMR spectrum of 2-ethoxy-2-(3'-methoxy-4'-allyloxy-phenyl)ethan-1-ol (**47**) in $CDCl_3$.

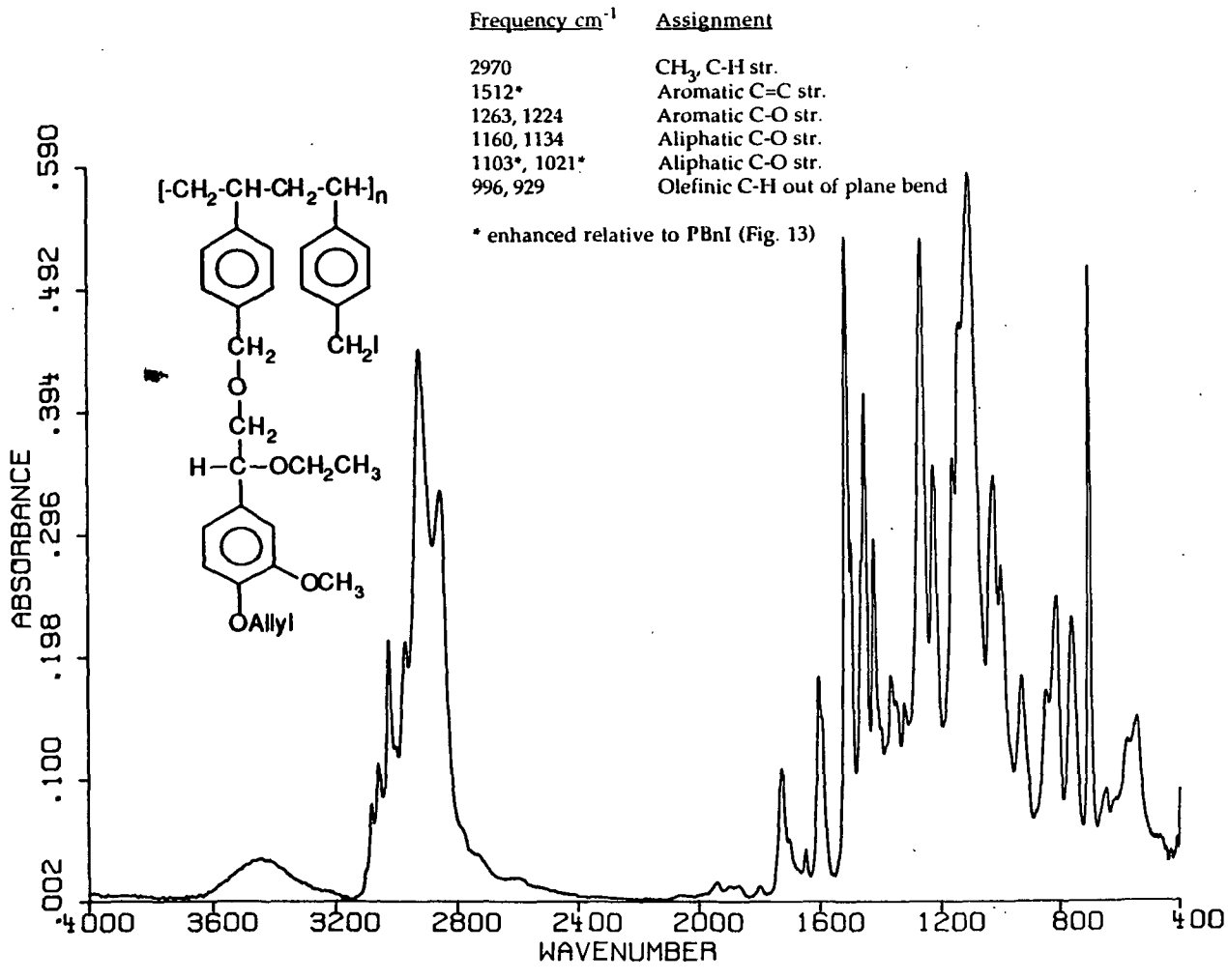


Figure 29. Infrared spectrum of heterogeneous QM intermediate 48.

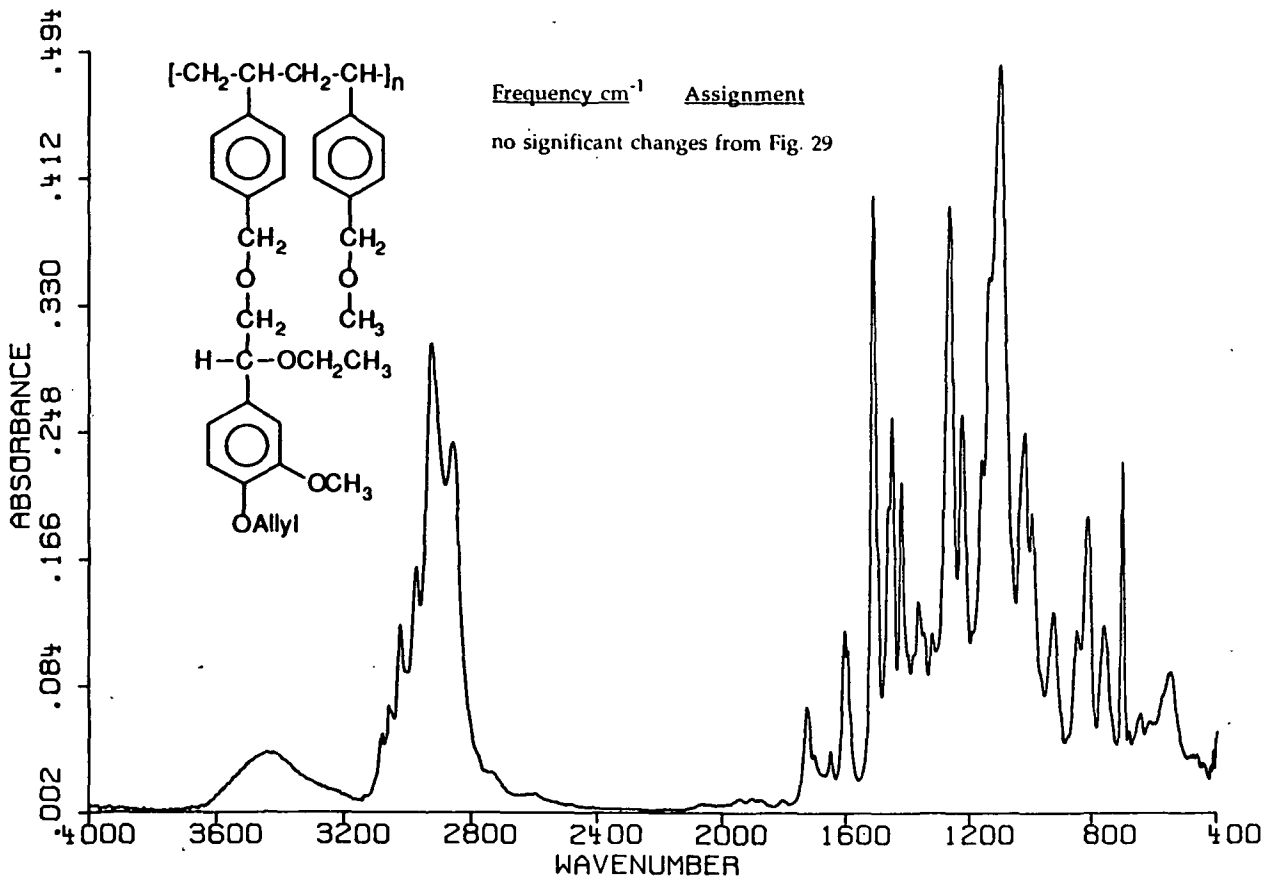
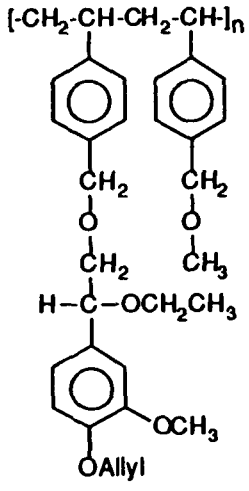


Figure 30. Infrared spectrum of methoxylated heterogeneous QM intermediate **48**.



15.6 ($OCH_2\underline{C}H_3$)
40.4 (polystyrene CH)
40-47 (polystyrene CH_2)
56.3 (OCH_3)
64.6 ($O\underline{C}H_2CH_3$)
69.8 ($ArO\underline{C}H_2$, $ArCH_2$, β-CH_2)
80 (ArCH)
113 (broad, $C_{2',5'}$)
117.9 ($=CH_2$)
128.3 (polystyrene omp Ar, $C_{1'}$)
133.5 (CH=)
149 (broad, polystyrene ipso, $C_{3',4'}$)
the signal for $ArCH_2O\underline{C}H_3$ is presumably at 56 ppm.

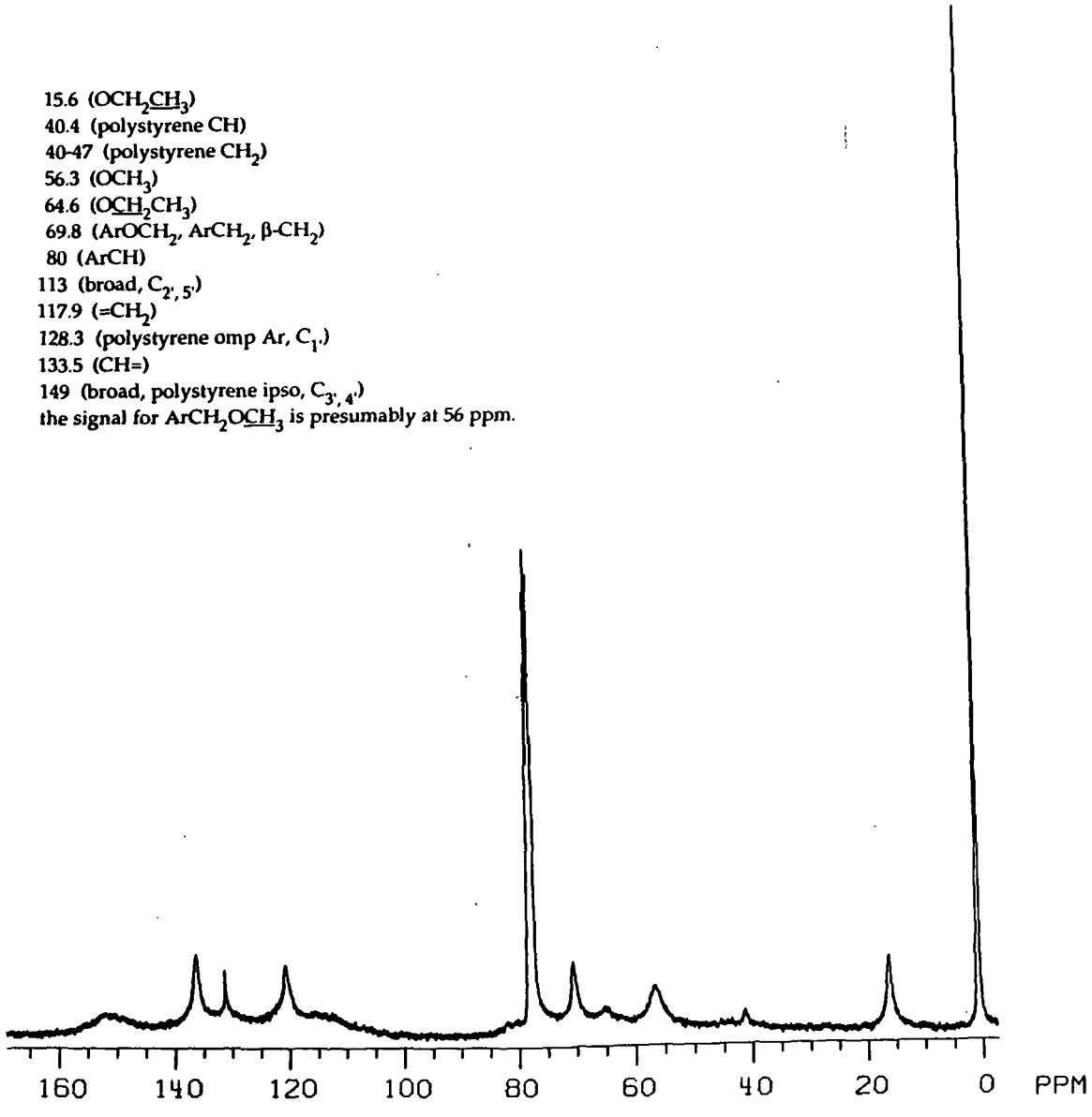


Figure 31. High resolution ^{13}C-NMR spectrum of heterogeneous QM intermediate **48** in $CDCl_3$.

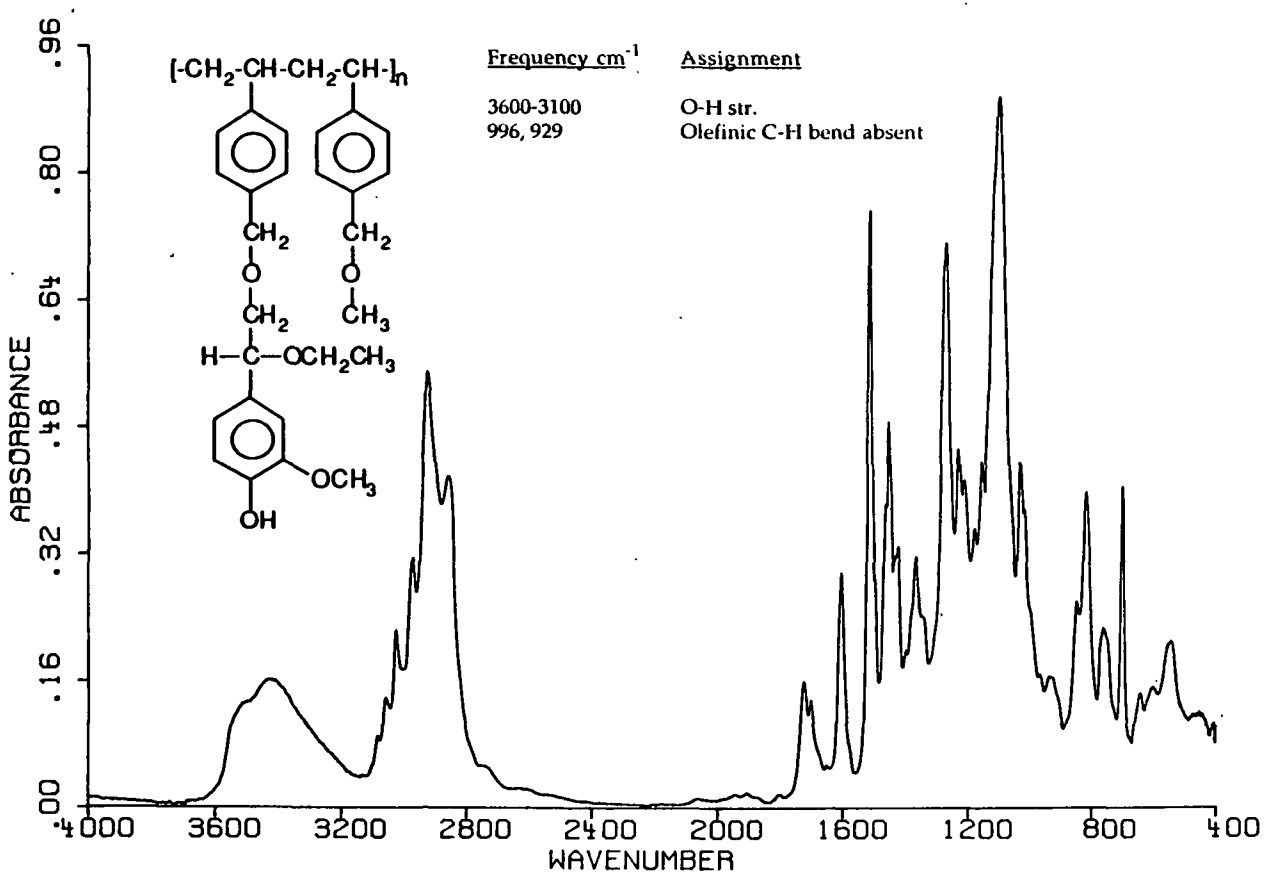
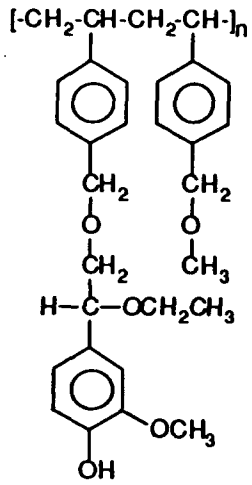


Figure 32. Infrared spectrum of polymer-supported QM model **49**.



The high resolution ^{13}C-NMR of **49** showed greatly reduced signals, relative to **48**, at 70, 118, and 134 ppm which confirms that the allyl group was effectively removed.

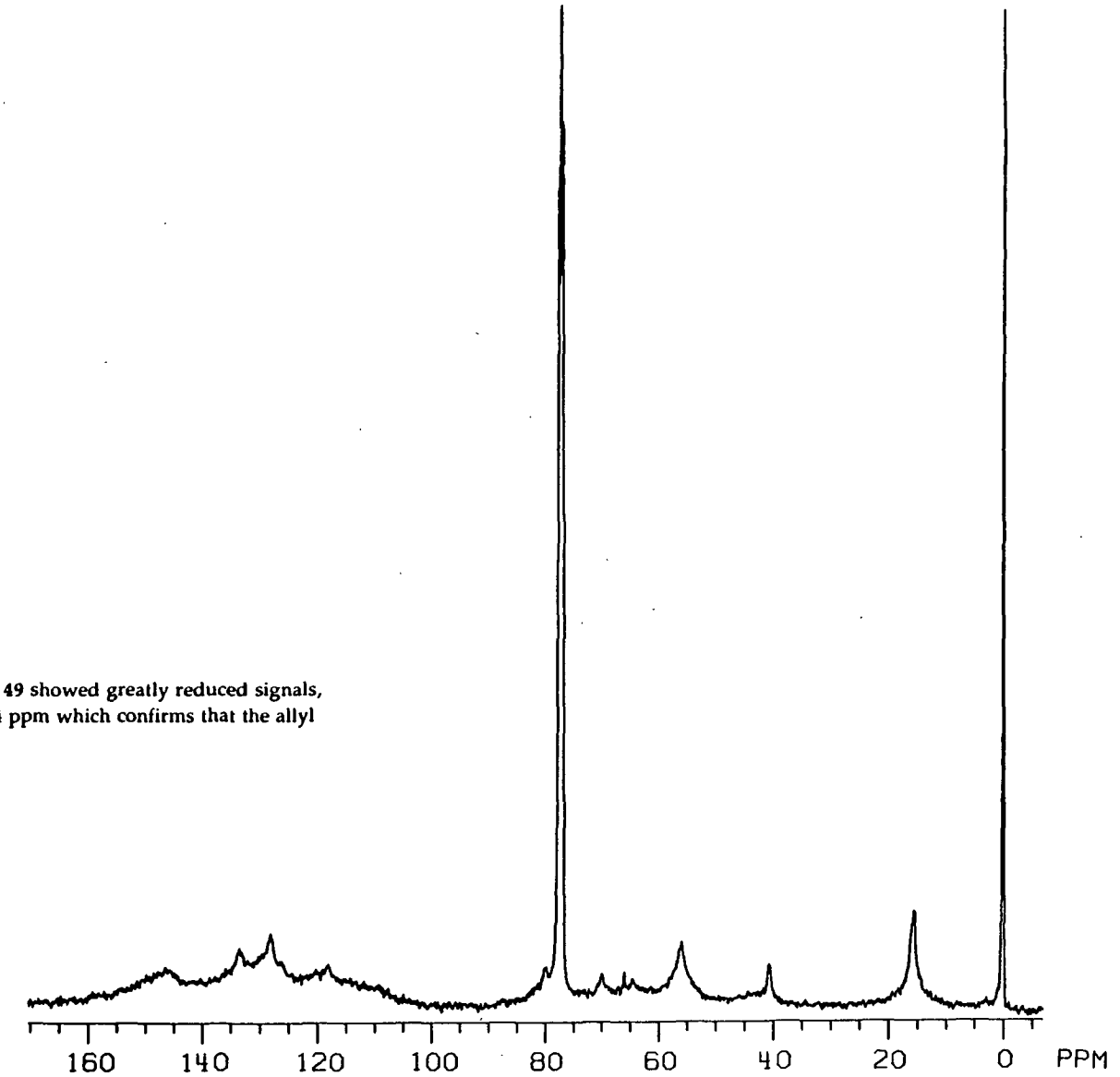


Figure 33. High resolution ^{13}C-NMR spectrum of heterogeneous QM compound **49** in $CDCl_3$.

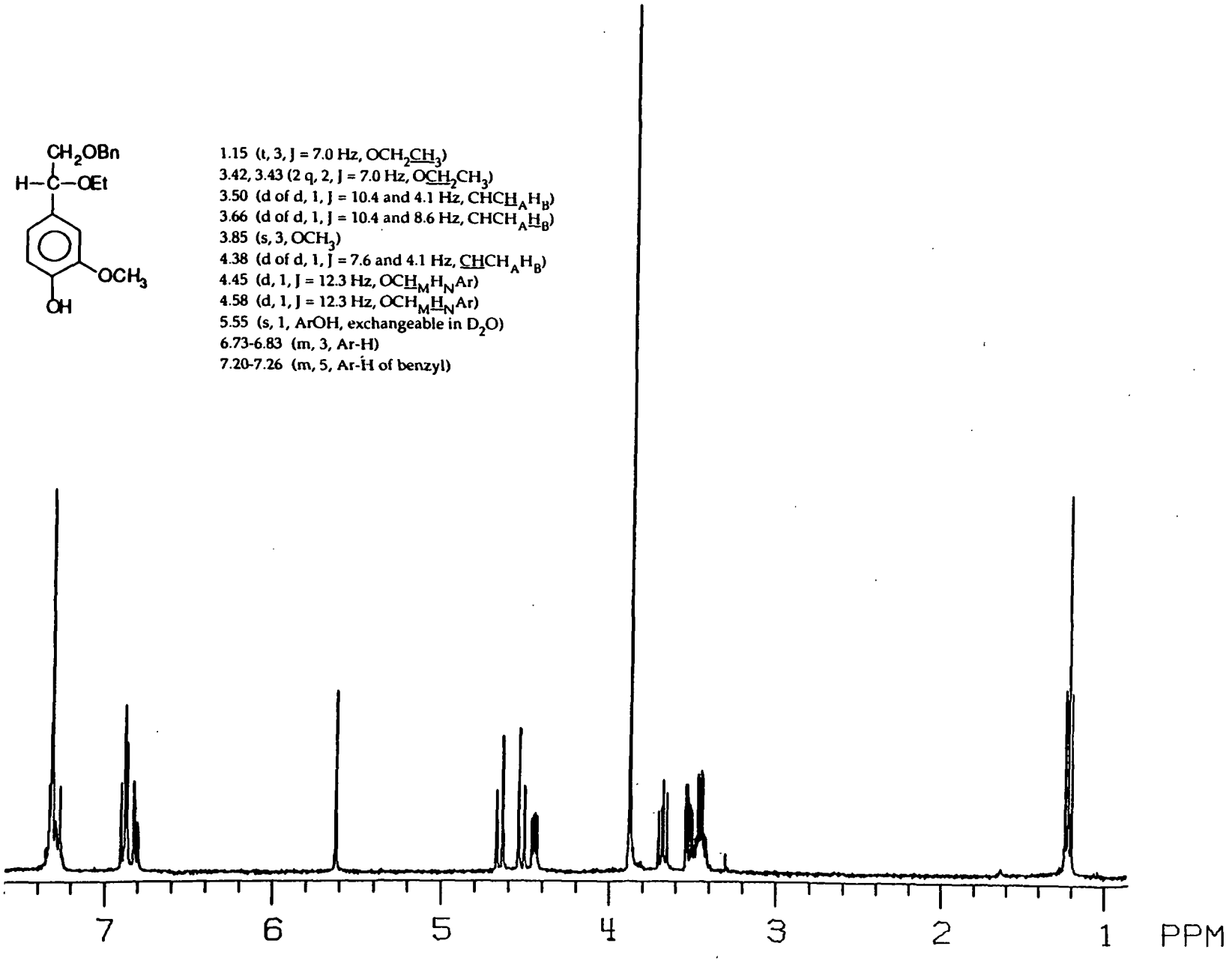
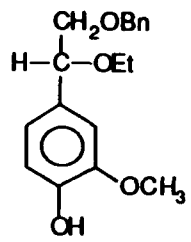


Figure 34. ^{1}H-NMR spectrum of 1-ethoxy-1-(3'-methoxy-4'-hydroxyphenyl)-2-benzyloxyethane (**80**) in $CDCl_3$.



15.4 (q, $OCH_2\underline{C}H_3$)
55.9 (q, OCH_3)
64.4 (t, $O\underline{C}H_2CH_3$)
73.4, 74.8 (2 t, $CH\underline{C}H_2$ and $ArCH_2$)
81.2 (d, ArCH)
109.0 (d, $C_{2'}$)
114.0 (d, $C_{5'}$)
120.1 (d, $C_{6'}$)
127.5 (d, C_4 of benzyl)
127.7 (d, $C_{3,5}$ of benzyl)
128.3 (d, $C_{2,6}$ of benzyl)
131.9 (s, $C_{1'}$)
138.4 (s, C_1 of benzyl)
145.3 (s, $C_{4'}$)
146.6 (s, $C_{3'}$)

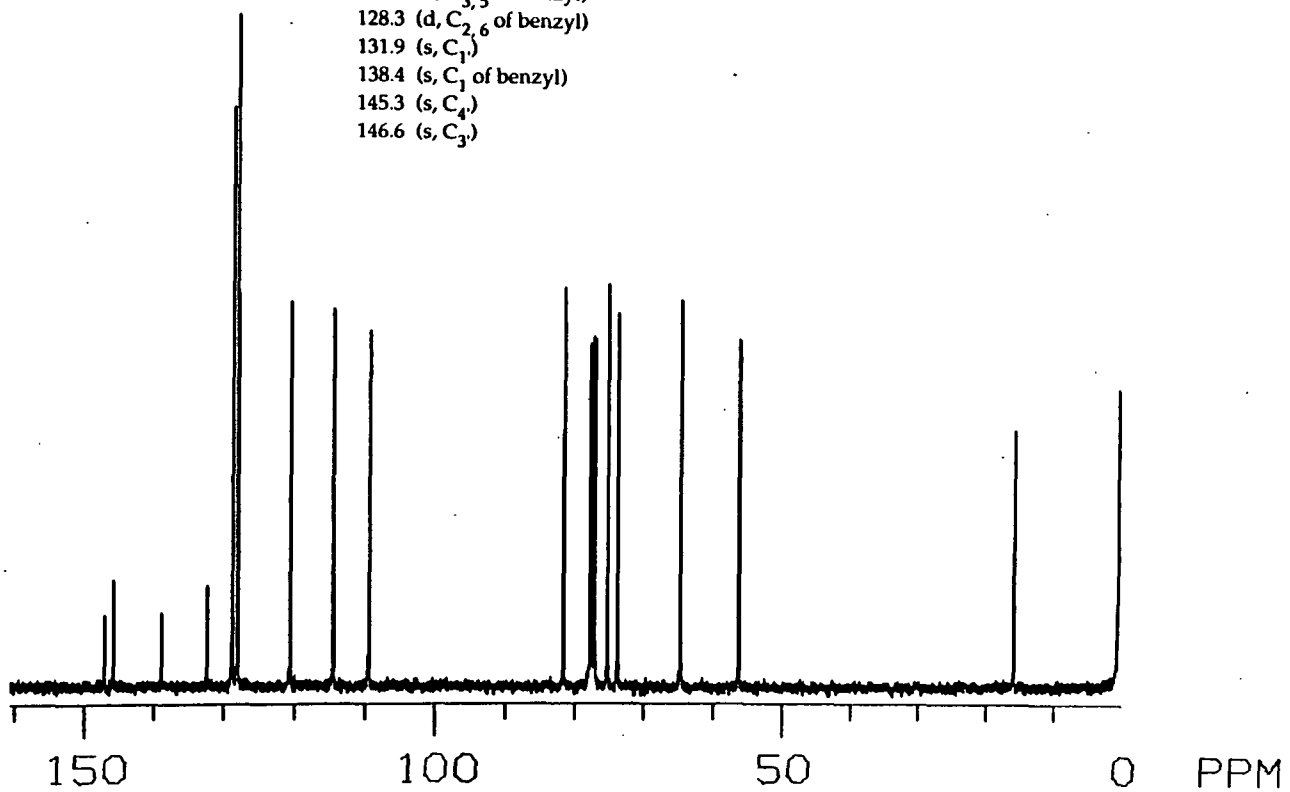


Figure 35. Decoupled ^{13}C-NMR spectrum of 1-ethoxy-1-(3'-methoxy-4'-hydroxy-phenyl)-2-benzyloxyethane (**80**) in $CDCl_3$.

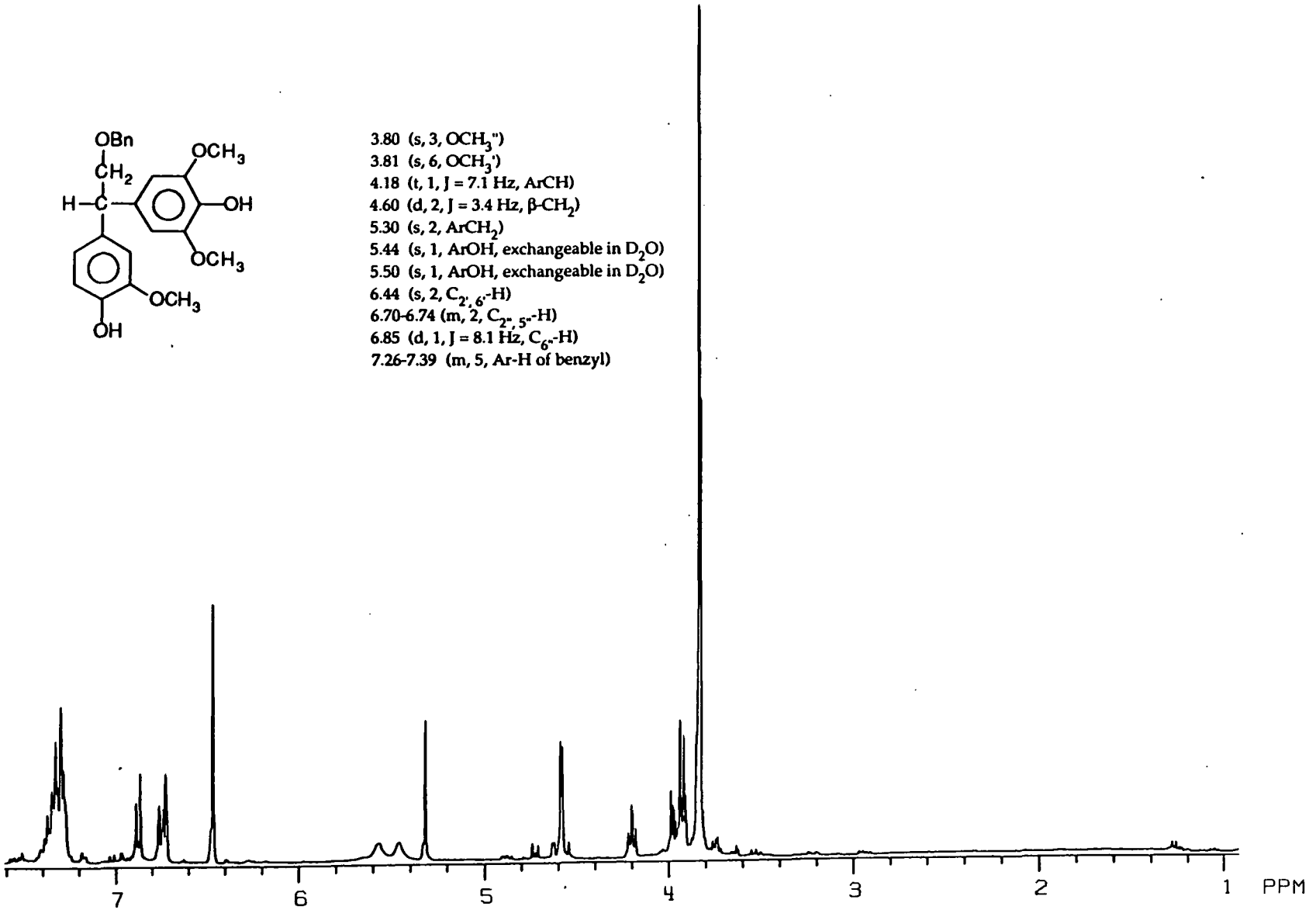


Figure 36. ^{1}H-NMR spectrum of 1-(3',5'-dimethoxy-4'-hydroxyphenyl)-1-(3"-methoxy-4"-hydroxyphenyl)-2-benzyloxyethane (79) in $CDCl_3$. The material contained a GLC detectable contaminant which is apparent in the 3.89-3.97 ppm region.

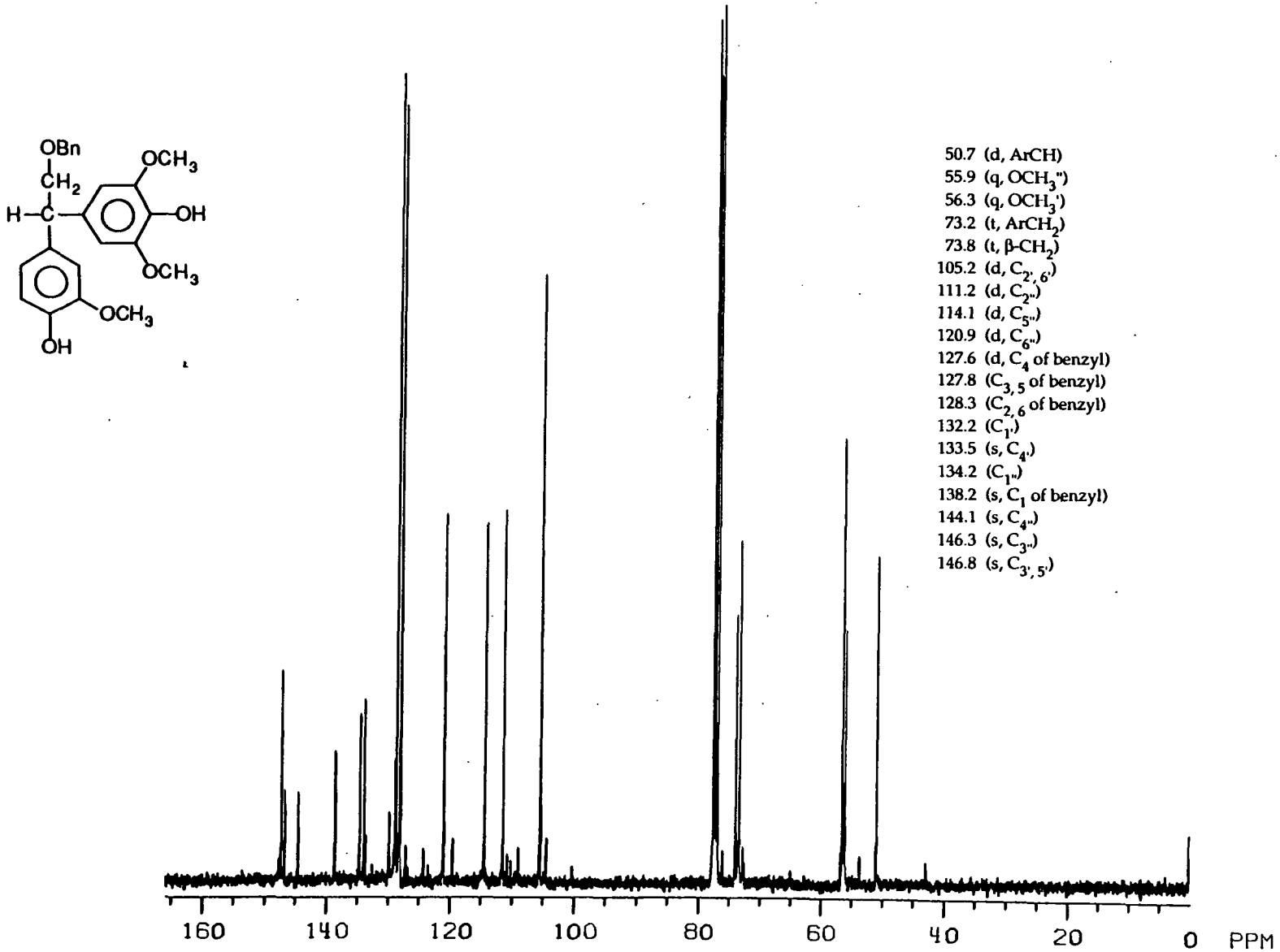


Figure 37. Decoupled ^{13}C-NMR spectrum of 1-(3',5'-dimethoxy-4'-hydroxyphenyl)-1-(3"-methoxy-4"-hydroxyphenyl)-2-benzyloxyethane (79) in $CDCl_3$. The material contained a GLC detectable contaminant which exhibits signals in the benzyl ring carbon region (125-130 ppm).

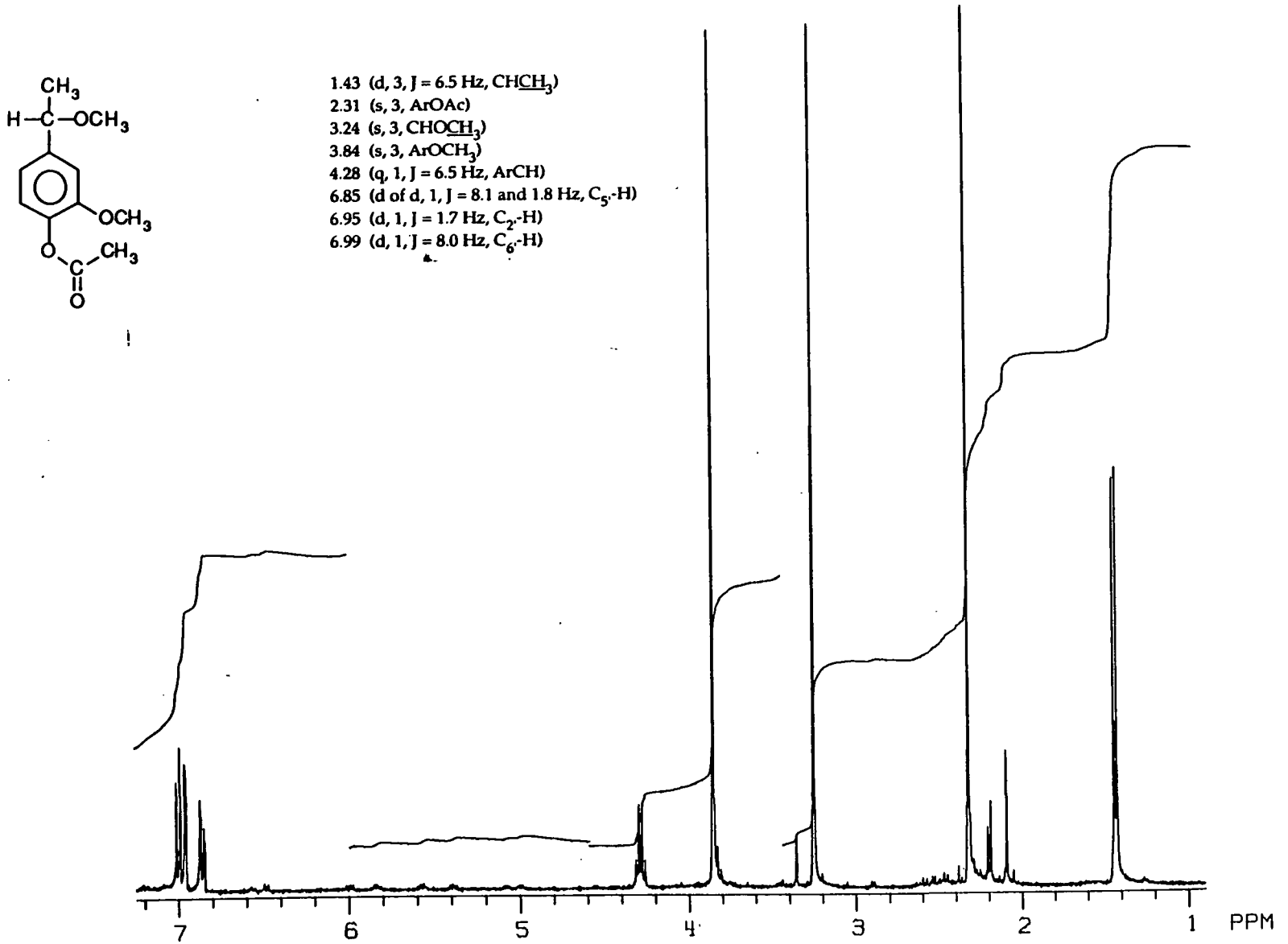
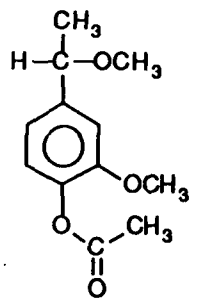


Figure 38. ^{1}H-NMR spectrum of 1-methoxy-1-(3'-methoxy-4'-acetoxyphenyl)ethane (68) in $CDCl_3$.



20.7 (q, $CH_3C=O$)
24.0 (q, $CH\underline{CH_3}$)
55.9 (ArOCH_3)
56.6 (q, CHO$\underline{CH_3}$)
79.4 (d, ArCH)
109.8 (d, C_2)
118.5 (d, C_6)
122.5 (d, C_5)
138.9 (s, C_1)
142.5 (s, C_4)
151.2 (s, C_3)
169.1 (s, C=O)

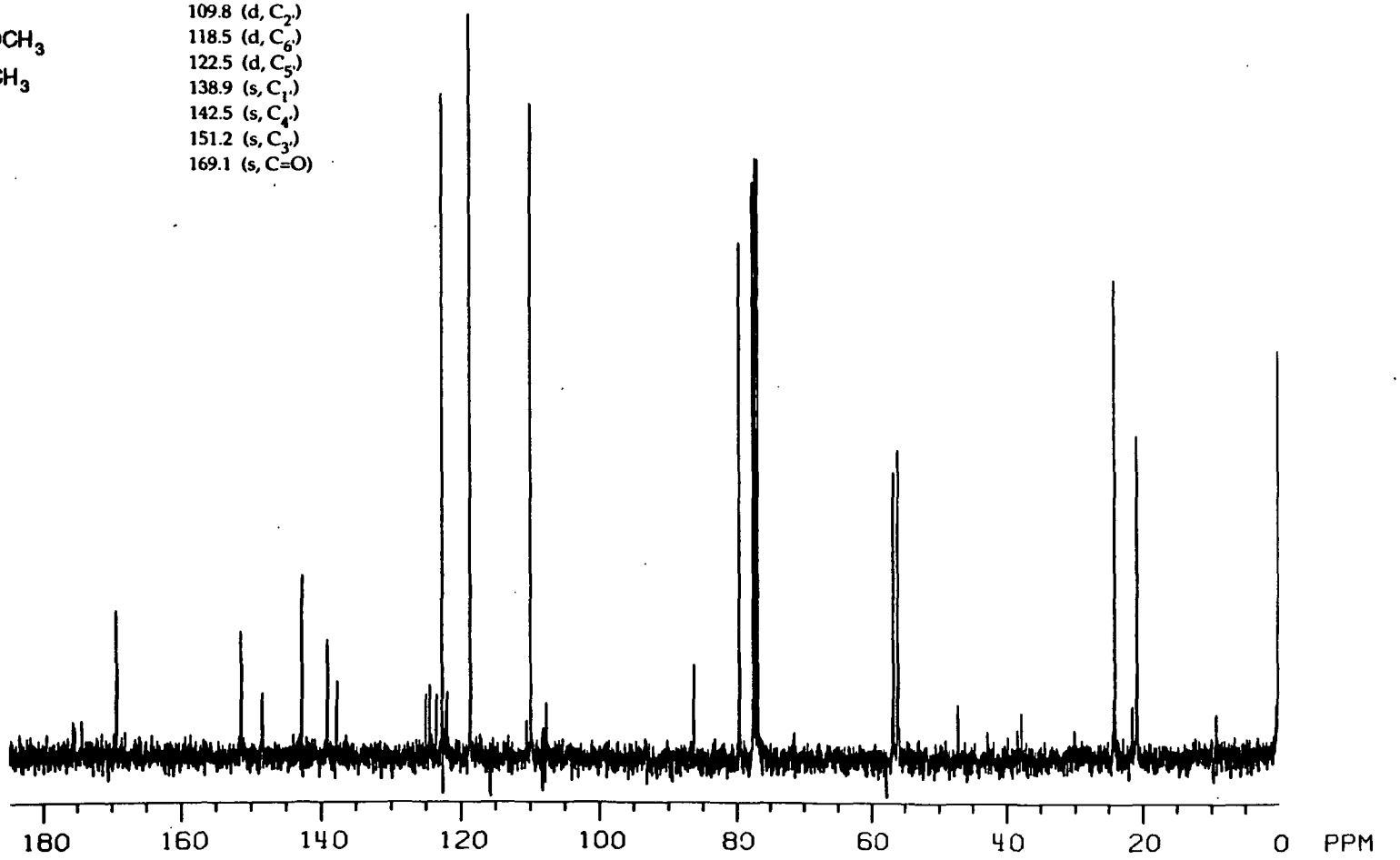


Figure 39. Decoupled ^{13}C-NMR spectrum of 1-methoxy-1-(3'-methoxy-4'-acetoxyphenyl)ethane (**68**) in $CDCl_3$.

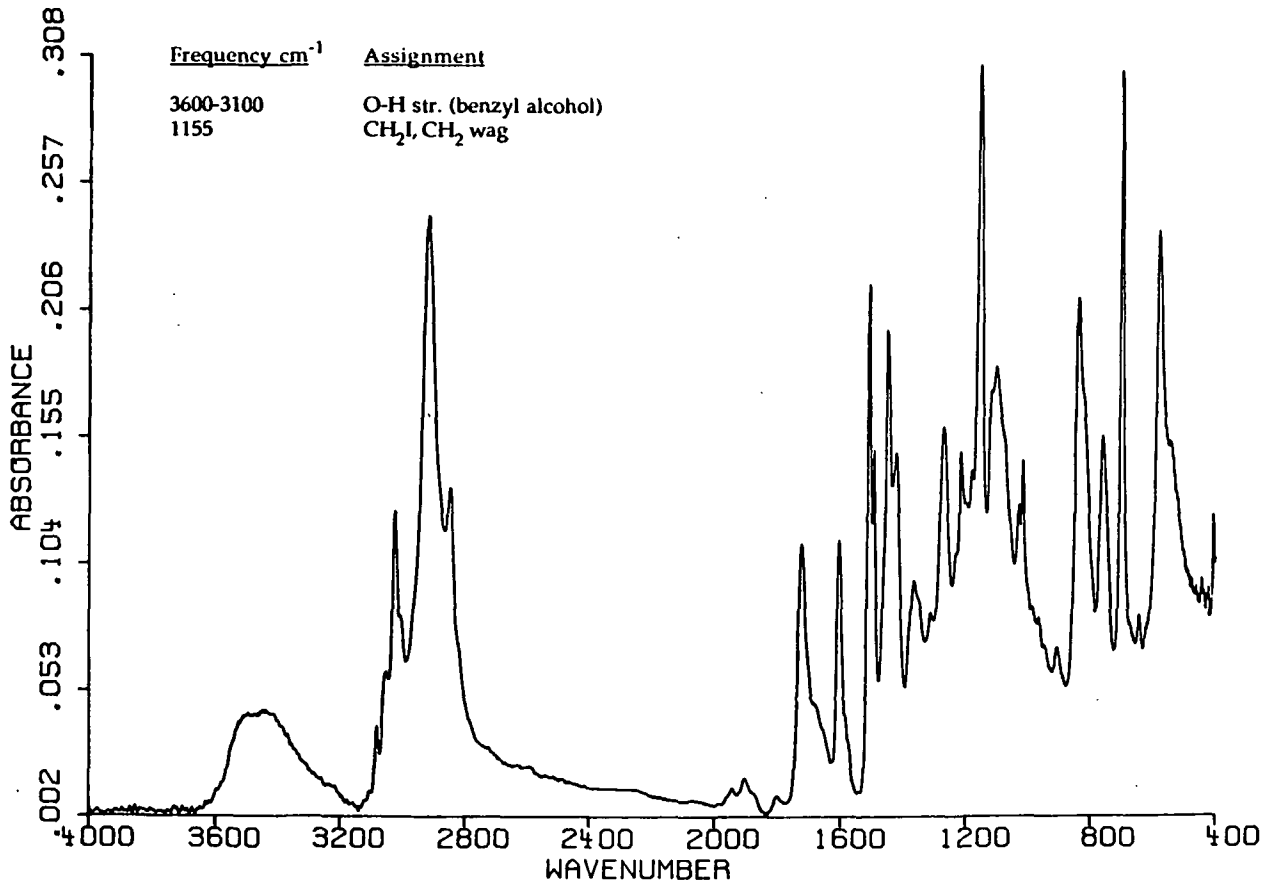


Figure 40. Infrared spectrum of **49** after treatment with iodotrimethylsilane.

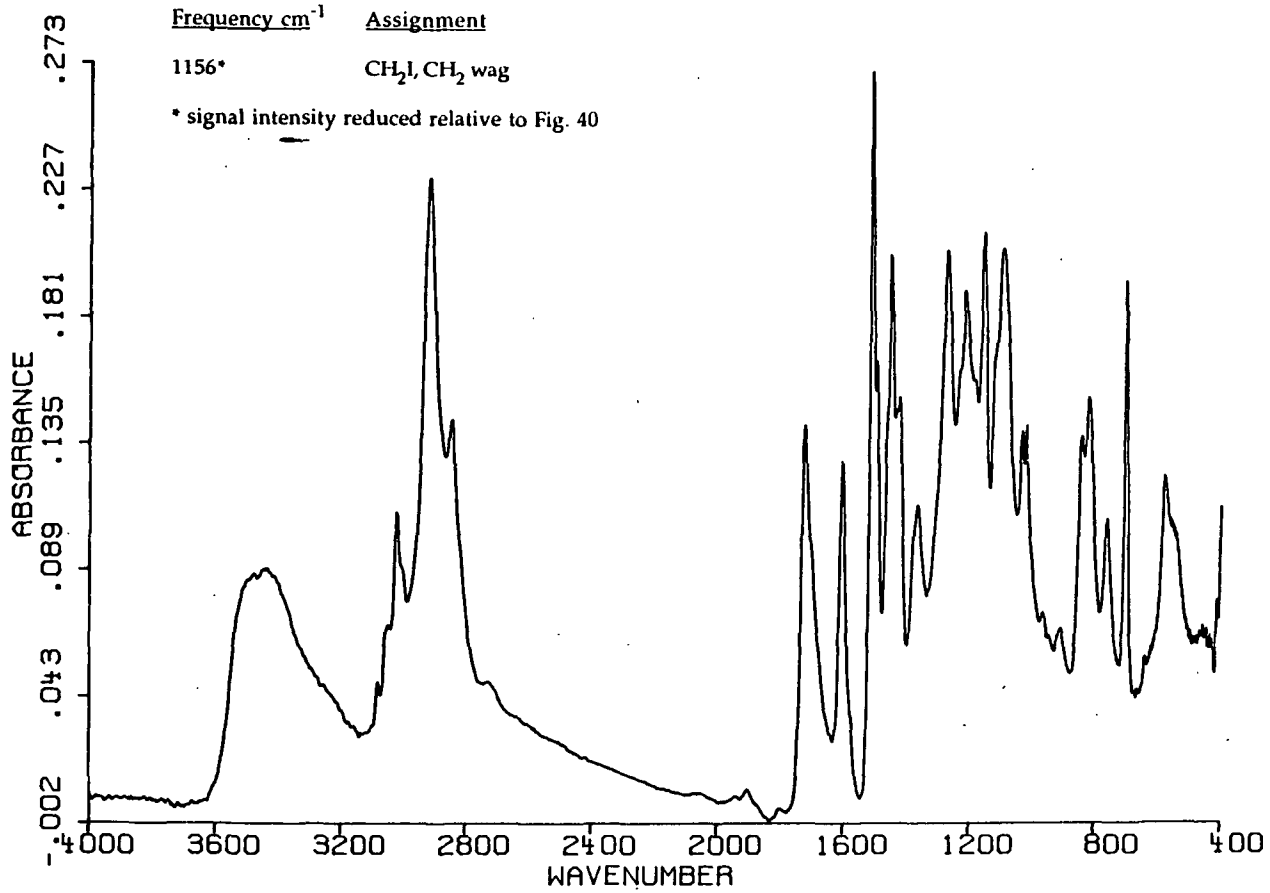


Figure 41. Infrared spectrum of soda cooked (1M NaOH, 40 min) **49** after treatment with iodotrimethylsilane.

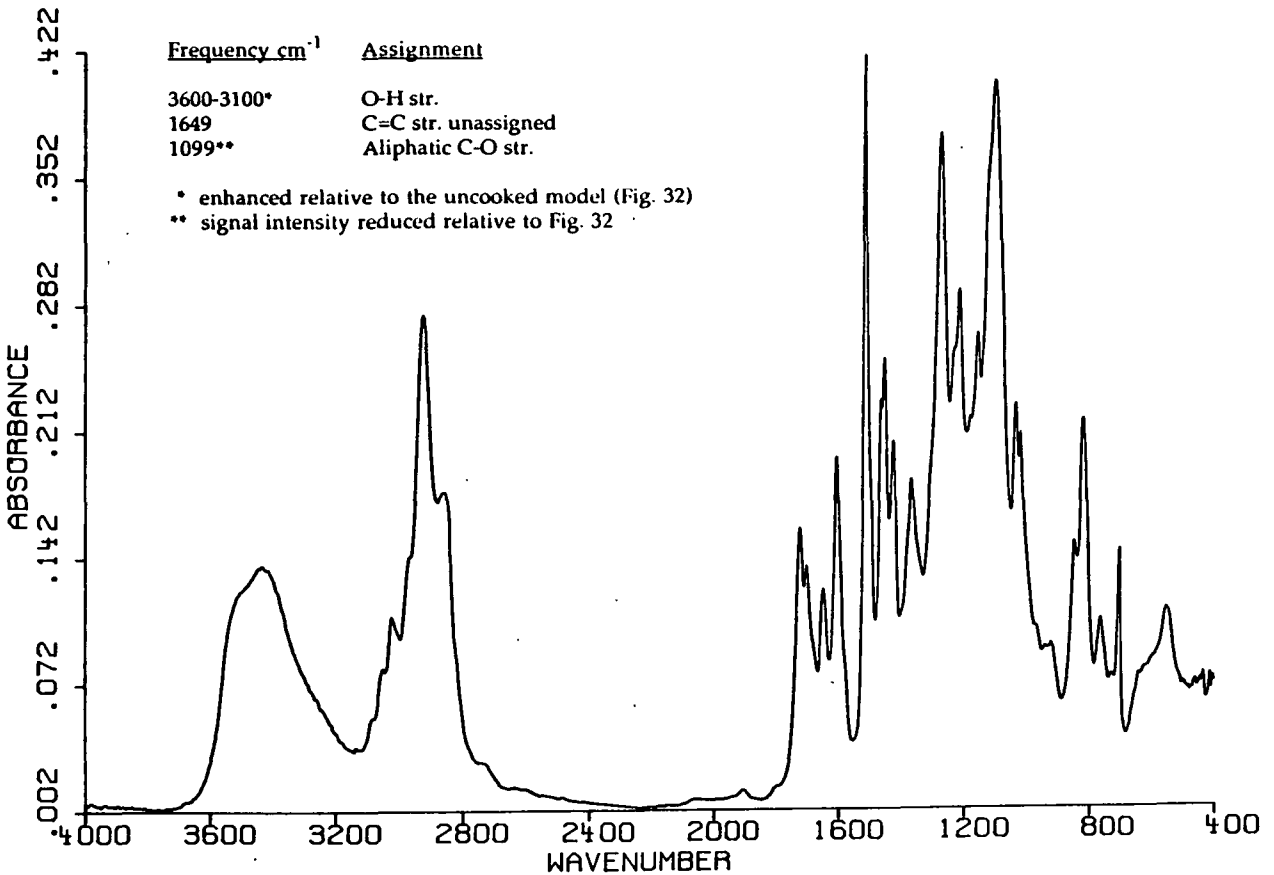


Figure 42. Infrared spectrum of reacted **49** (2 hr., 0.05M NaOH, 168 °C, 3 eq. syringol).